INTERNATIONAL ATOMIC WEIGHTS, 1943

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	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

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INTRODUCTORY GENERAL CHEMISTRY

INTRODUCTORY
GENERAL CHEMISTRY

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YALE UNIVERSITY

THIRD EDITION

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Third Edition

PREFACE

The fundamental objectives of the course in general chemistry for students in a first course in this subject are: to afford an understanding of the scientific method of thought by coordinating the facts, laws, and theories of chemistry in an orderly science; to develop a rational basis for an appreciation of the true significance of chemistry in the modern world; and to present the basic material required for more advanced courses.

Since chemistry is a science founded on experimental data, facts acquired by observation are discussed prior to the development of theories advanced for the interpretation and correlation of these facts. The theories are then applied in the consideration of additional data that their usefulness and limitations may be understood. Theories are not to be regarded as ends in themselves for they are useless unless they find application to the subjects under consideration. Changes in the order of some of the topics have been made in the preparation of this edition in order to simplify and improve the presentation of the subject. Thus, the atomic theory of Dalton follows the discussion of changes in substances and permits the introduction of symbols, formulas, and simple equations early in the course. The postulates of this theory are adequate for the correlation of a number of important points encountered at the beginning of the course. The discussion of the structure of the atoms comes later, Chapter 13, after the study of the alkali metals and halogens has given a basis for the periodic system and presented material to which the assumptions of the theories are applicable.

Chemical equilibrium is discussed in Chapter 8, following the physical equilibria involved in changes of state and in solutions. The earlier inclusion of these principles simplifies their application subsequently in the consideration of ionic equilibria and industrial processes.

The sequence in the topics, atomic structure, ionization, elec-

trolysis and electric cells, ionic reactions, acidity, basicity, ampho-
lytes, hydrolysis, affords a unified treatment of modern theory and
its applications to chemical phenomena. The ionic structure of
crystalline salts makes logical their direct dispersal by water to
form ionic solutions in which the activities of ions are affected by
inter-ionic forces and by hydration of ions. The ionization of molec-
ular acids is attributed to interaction between solute and solvent.
Acidity and basicity are discussed in terms of the Brönsted general-
ized definitions which are then applied consistently throughout
the remainder of the book. Through the use of these definitions,
great simplification is secured in the discussion of acids, bases,
ampholytes, and hydrolysis, since the process of proton transferal
is common to many of the reactions involved. Emphasis is placed
on the fundamental nature of the changes, not on the symbolism
involved in their representation. The author does not consider the
formulation of hydronium ions, or of other hydrated ions, in equa-
tions a matter of importance, except in those instances in which
some end is attained by the inclusion of water of hydration. The
application of these definitions to solutions in solvents other than
water does not come within the scope of this text.

The application of the principles dealing with ionic phenomena
to analytical separations affords a rational view of the procedures
involved. Specific reactions for the detection of ions are not, in
general, emphasized because they come more properly within the
field of the individual laboratory work of the student. This chapter
is not intended for direct assignment as a unit, and may be omitted
altogether without interrupting the continuity of treatment.

The discussion of the elements and their compounds is based on
the classification according to atomic numbers. Following the
main groups, four chapters deal with transition elements. A chapter
has been included giving a general discussion of the metallic ele-
ments and the principles involved in their production from the
different classes of ores. In the sections dealing with the production
of specific metals, diagrammatic outlines have been introduced
to show the essential steps required.

The chapters in which the organic compounds are discussed
have been enlarged by the inclusion of a greater number of the
typical classes of substances.

An understanding of the applications of chemistry in the arts and industries can be acquired only through a knowledge of the properties of substances which suit them to their varied uses. References to the practical uses of many substances, together with the more detailed description of certain selected processes, serve to emphasize these practical aspects. Figures showing the production and consumption of a number of substances have been quoted from *Chemical and Metallurgical Engineering*. Information regarding the production of a number of strategic materials is not available.

Pictures of eminent scientists and of industrial plants have been omitted in this edition. Such material can be presented more effectively through the use of slides and motion pictures, and by reference to journals, magazines, and books.

Lists of supplementary readings at the ends of the chapters suggest further study along historical, philosophical, and industrial lines. Additional references to more recent articles in the *Journal of Chemical Education*, *Journal of Industrial and Engineering Chemistry*, *Chemical and Metallurgical Engineering*, *Chemical and Engineering News*, and other journals are suggested to keep these lists up to date.

The exercises at the ends of the chapters are intended to direct the attention of the student to specific topics as an aid in the preparation of his own outline and in checking his mastery of the subject under consideration. The section on problems at the end of the book has been enlarged. The tables in the appendix furnish data in readily accessible form. They are for the most part based on *Handbook of Physics and Chemistry* (Chemical Publishing Company, Cleveland); Latimer and Hildebrand, *Reference Book of Inorganic Chemistry* (The Macmillan Company, New York); and *International Critical Tables* (McGraw-Hill Book Company, New York).

For helpful suggestions and criticism, the author wishes to express his appreciation to his associates in the courses in general chemistry in this University, Professors H. G. Dietrich, D. T. Keach, E. B. Kelsey, Dr. E. W. Fager, and Dr. E. J. King; to Professor J. A. Timm, Simmons College; to Professor W. C. Sumpter, Western Kentucky State Teachers College; and to Professors R. B. Conklin and D. D. Wright, Brooklyn College.

                                                    Stuart R. Brinkley

New Haven, Connecticut

CONTENTS

INTRODUCTORY GENERAL CHEMISTRY

Chapter 1

INTRODUCTION. VARIETIES OF MATTER

The material environment in which a person lives exerts a profound influence upon his habits of life and thought. Observation leads one to note continual changes in the material environment. Many of these changes occur in response to natural agencies; while others are the result of special conditions established by human agencies.

We have no way of learning prehistoric man's thoughts about the nature of matter and natural phenomena. We do know, however, that superstitions and myths resulted from wonder and fear caused by phenomena which were not understood. With the accumulation of specific knowledge, the powers of observation and interpretation have been developed and improved, and it has become clear that there is a regularity and order in natural events, and that changes in natural conditions lead inevitably to certain uniform responses.

Natural Sciences. Complete and accurate knowledge concerning changes is secured through careful observation and exact measurement. Changes involving identical materials and conditions always produce the same results. This is one of the fundamental principles of science, because our understanding of the law and order to which the material world is subject depends on the reproducibility of factual observations. Generalities become apparent from facts, classified in an orderly manner. *A natural science is a systematic body of knowledge dealing with natural substances and the changes which they undergo.* The more clearly causes and effects of natural phenomena are understood, the more successfully may they be applied to practical ends. An appreciation of the true significance of science in the modern world comes only from an understanding of the interrelation of scientific phenomena.

The Scientific Method. The methods of study and reasoning employed by science are important in other branches of knowledge

also. The most important contribution of science to the intellectual life of the modern world is the development of the scientific method. The basis of this method is a recognition of the significance of facts, acquired by experimental observations, as the foundation of knowledge rather than conclusions based on intuitive reasoning. This does not mean that imagination has no place in science. To the contrary, imaginative and intuitive processes are highly important. Nevertheless, imagination must be controlled, and intuitive conclusions must be checked by experimental observations to establish their validity.

Experimental Data. The first step in the scientific method is the observation of facts. Until the seventeenth century the importance of experimental observations was not commonly grasped; and, indeed, it is not yet fully appreciated by the general public. The Greek philosophers based their ideas about the nature of matter and its changes on observed facts to only a limited extent. During the Middle Ages, however, some thinkers were fully aware of the value of experimental science. Roger Bacon (about 1210–1294) understood clearly that one may obtain certainty in science only by experimental methods. Leonardo da Vinci (1452–1519), best known as a painter and sculptor, was also preëminent as an engineer, architect, physicist, and biologist. He approached science from its practical aspects, because he recognized that the solution of his problems depended on the actual behavior of the materials with which he dealt and not on opinions concerning the way they should behave.

The experimental method involves careful observation of phenomena which occur in nature and also of those which result from planned experiments. The data must be as complete as experimental difficulties permit. Sound judgment based on broad experience must be exercised, and limitations in the accuracy of the measurements must be recognized. Personal prejudice must be excluded, and preconceived notions must be discarded or modified if they are found to be out of accord with the experimental data.

Scientific Laws. The second step in the scientific method is the classification of data. Single experiments lead to more or less unrelated specific facts. If, however, the experiments are planned so that they deal with a series of related substances or phenomena

and are carefully performed, it naturally follows that the data are related. The investigator now classifies these related data and, by inductive reasoning starting with particular instances, may develop generalizations or laws. *A scientific law is a statement which summarizes a large number of exact experimental observations.* Scientific laws are essentially descriptive. Consequently, they are not more accurate than the experiments on which they are based, and are not more widely applicable than the observations and calculations by which they may be tested.

Theories. A third step in the scientific method is the explanation and interpretation of data. However, the scientific meaning of the word "explain" must be understood. A fact is commonly explained by showing that it is a particular instance covered by a general law which is universally accepted. In dealing with scientific facts, this type of explanation is frequently not possible because of lack of information on more fundamental laws. Therefore, after scientific laws have been established, an hypothesis is advanced in an attempt to account for the facts. *An hypothesis is a supposition concerning the structure of matter or the mechanism of observed changes* that aids in visualizing and interpreting the data. Hypotheses which are found to afford a satisfactory interpretation of all of the facts involved and to account also for new facts of a related nature, as they are discovered, are accepted as theories. *A theory is a model or mental picture by which scientific laws may be coordinated and interpreted.* Theories differ from laws in that they employ concepts which are not subject to direct observation and proof. As new facts are discovered, the inadequacy or incorrectness of a theory may become apparent. Thus modifications in the theory are required, or the theory may be abandoned. Improvements in experimental methods and increase in the amount of knowledge serve as tests of the usefulness and validity of theories. It is assumed by scientists that a firmly established theory actually provides a correct model, but it is also fully understood that changes in the model may become necessary.

A fourth significant factor in scientific method is the use made of theories in planning research for the discovery of new facts. By deduction from accepted theories, conclusions are reached which must be tested experimentally. The scientific method is a complex procedure, involving inductive reasoning which leads to the great

principles of science and deductive reasoning by which these principles are employed in the discovery of new knowledge and the development of understanding.

Subdivisions of Science. The amount of knowledge concerning scientific phenomena and principles is now so great that it is desirable to subdivide science into several branches. Although the spirit of science is the same for all of its branches, the specific vocabulary and the experimental procedures of one field of science may not be suited to some other field. *The physical sciences* deal with inanimate objects; *the biological sciences* with living organisms and their products. Further subdivisions are made arbitrarily to limit the field under consideration and to group together facts, laws, and theories that are applicable to specific branches of science. Thus, chemistry, physics, and geology are physical sciences, while botany, zoology, and physiology are biological sciences. It is important to remember that these subdivisions are made arbitrarily, and that the branches of science are portions of a great body of knowledge in which there are no natural divisions. The sciences overlap so that a number of topics appear in the considerations of more than one subdivision. The branches of science should be integrated as fully as the stage of understanding permits. In many instances this integration is not possible until a rather large body of knowledge has been mastered.

Chemistry is the branch of science which deals with different substances or varieties of matter. There are a number of aspects of chemistry, which receive emphasis in the different courses of study in this subject. Inorganic chemistry deals with mineral substances and the changes which they undergo. Organic chemistry involves primarily the compounds of carbon. When this name was first introduced, it was believed that these compounds could be formed only under the influence of living organisms. Although this belief was shown to be incorrect, the name has been retained. The majority of these compounds are still secured from products of living organisms, but many of them may now be prepared from other source materials. Analytical chemistry includes methods and principles that are applied in the separation, detection, and measurement of the quantities of different substances. Physical chemistry deals with theoretical problems, frequently in the borderland between

physics and chemistry, and represents the behavior of substances in exact mathematical terms in so far as it is possible to do so. Chemical engineering is the branch of the subject that involves engineering problems met in carrying out chemical operations on an industrial scale. An introductory course includes topics from all of these phases of chemistry. The study of descriptive chemistry is basic to knowledge concerning the behavior of typical varieties of matter, and it serves as a foundation for the laws and theories of the science. Industrial and economic applications show the importance of chemistry in the modern world. General chemistry furnishes a survey of the science and a basis for an understanding of the methods of science.

Matter. No single set of properties is sufficient to serve for the definition of matter. Many speculations concerning its ultimate nature have been advanced but have failed to satisfy the inquiring mind. It is necessary, therefore, to accept the fact that matter is an objective reality, but that we have no definite knowledge which enables us to state precisely what matter is. We may, however, study particular varieties of matter and learn a great deal about the nature of these specific substances. From such knowledge, we may then arrive at an understanding of the nature of the units of structure, which are common to all varieties of matter.

Mass is the quantity of matter in a particular specimen. The mass of an object depends on its inertia, *i.e.*, the resistance which it offers to a change in motion. There are no direct units for the measurement of mass, but the relative masses of objects are determined by weighing them. Weighing an object consists in measuring the attraction between the object and the earth in arbitrary units. The gravitational
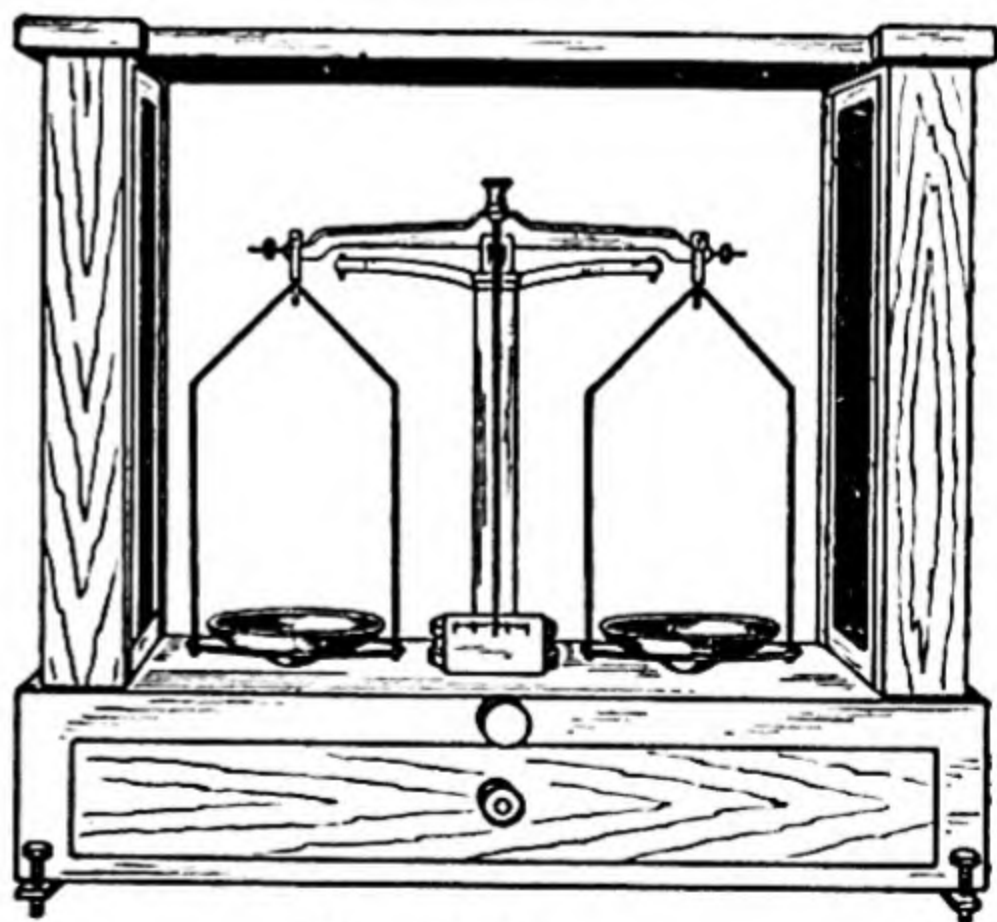

Fig. 1. Balance

attraction between two objects varies directly with their masses and inversely with the square of the distances between their centers. At the same distance from the center of the earth, the masses

of two objects are directly proportional to their weights. The object to be weighed is placed on the left pan of the balance (Fig. 1), and the weights are placed on the right pan until the object is counterpoised. In this manner, the mass of the object is measured in arbitrarily selected units of weight. The unit of mass is the *gram*, a thousandth part of the mass of the standard kilogram. The standard kilogram represents the mass of one liter of water at 4° C.,* the temperature at which water has greatest density; and one gram is the mass of one milliliter of water at 4°. This is almost the same as the mass of one cubic centimeter of water at this temperature.

Energy. Matter and energy are so closely related that the study of one necessarily involves a consideration of the other. Changes in matter are accompanied by changes in energy, and may occur in response to changes in energy. *Energy is the capacity of a body to do work.* There are a number of forms of energy. The kinetic energy of an object is energy due to its motion, and potential energy is energy due to position. Heat, light, and electricity are familiar forms of energy. Chemical energy is the energy an object possesses because of its composition.

Different units are employed for the measurement of different forms of energy. The unit of heat is *the calorie*, the amount of heat required to raise the temperature of one gram of water one degree at 15°. Temperature is an intensity factor in measuring heat, and the calorie is the quantity factor. The unit of electrical energy is the *joule*, which is equal to the product of the quantity unit, one coulomb, and the intensity unit, one volt. Kinetic energy is measured in *ergs*, the work done by a force of one dyne acting through a distance of one centimeter. The kinetic energy is equal to $\frac{1}{2} mu^2$, in which m is the mass in grams and u the velocity in centimeters per second. Chemical energy is manifested during changes in composition, usually in the form of heat. Hence, chemical energy is usually expressed in terms of the heat change to which it is equivalent.

One form of energy may be transformed into another. During the combustion of coal, chemical energy is transformed into heat.

* The temperature scale employed throughout this book is the centigrade scale unless otherwise specified.

The heat energy may be employed to produce steam to run an engine, which, in turn, may be used to drive a dynamo and generate an electric current. The current may be passed through a storage battery, where it causes changes in the composition of the substances in the battery and is thus converted into chemical energy again. Even though the amount of chemical energy stored in the battery is less than that of the coal and air with which the series started, careful measurements show that the total amount of energy involved in each of these transformations, — that usefully converted and that wasted because of lack of complete efficiency in the machines, — is constant. This experimental conclusion may be stated in the form of the **Law of Conservation of Energy: The total amount of energy undergoing transformation from one form to another in a closed system is constant.** This law, first expressed by Helmholtz in 1847, is one of the most important and far-reaching generalizations in science, but it is not considered to be a universal principle, but rather to apply as an experimental generalization to complete limited systems.

There is an exact relation between energy and work. The equivalence of the two was established by Joule, whose experiments on the mechanical equivalent of heat led to the value:

$$1 \text{ calorie} = 4.183 \times 10^7 \text{ ergs} = 4.183 \text{ joules}$$

None of our machines gives a complete conversion of energy into useful work. Friction causes the transformation of some of the energy into heat, which becomes dissipated by conduction from one body to another, so that it is no longer available for further transformation. In natural phenomena, transformations continually lead to degradation of energy in this manner.

States of Matter. It is a familiar fact that matter exists in three states or forms. Thus, water is a solid, a liquid, or a gas, depending on the conditions of temperature and pressure. Most of the common substances may also be obtained in each of these states. The transition from one state to another occurs under definite conditions of temperature and pressure for each substance, and is accompanied by a change in energy. The solid is the familiar form of a substance at temperatures below its melting point; the liquid at temperatures between the melting and boiling points; and the gas at tempera-

tures above the boiling point. Heat is absorbed during the melting of a solid and during the evaporation of a liquid, and is evolved during the opposite changes. Some of the properties which are characteristic of matter in these different states and the phenomena which accompany the change of state are discussed in Chapter 5.

Substances and Their Properties. Substances are varieties of matter. *A substance is homogeneous, i.e.,* it has uniform composition throughout. A substance is characterized by a series of specific properties or attributes by which it may be recognized and described. The physical state in which a substance exists at ordinary temperature and pressure is a prominent property. The boiling point and the freezing point of a liquid, and the melting point of a solid, are definite temperatures characteristic of the substances. Other common properties are color, odor, taste, density, solubility in water, and conductivity of heat and electricity. A crystalline solid has definite structure.

The uses of substances depend on the properties they possess. One of the important uses of copper is due to the fact that it is a good conductor of electricity. Other properties contributing to its usefulness for transporting electrical power are its ductility, strength, and resistance to atmospheric corrosion. The fact that it may be obtained in greater quantity and at lower cost than other good metallic conductors, like silver, is not a property, but it may be decisive in the choice of copper for this purpose.

The chemical properties of a substance depend on its composition and the changes which it may undergo. Instability toward heat is a chemical property of some substances, such as cane sugar, which decompose when heated. Other chemical properties may involve the interaction of two or more substances. The combustibility of carbon in air is a chemical property of the carbon and also of the oxygen in the air.

Classification of Substances. Different varieties of matter may be classified according to their composition and properties. Many materials are not uniform in composition but are composed of two or more varieties of matter having different properties. Such materials are not single substances but are heterogeneous mixtures. It is possible to distinguish the individual homogeneous particles in such mixtures. Each of the homogeneous materials of a single

variety in any sample of matter is a *phase*. There are two phases in a mixture of two solid substances. Similarly, there are two phases in a mixture of the solid and liquid forms of a single substance, and three phases if the gaseous form of the substance is present along with the other two forms. Homogeneous materials may be classified into elements, compounds, and solutions.

Elements. There are a number of substances which cannot be decomposed by ordinary chemical means such as the application of heat, the passage of an electric current, or interaction with other substances. These substances are chemically simple substances in that all of the particles that may be obtained from them by chemical processes of separation and subdivision behave in the same manner. *The chemical elements are chemically simple substances.*

There are a number of elements that decompose spontaneously, giving rise to high-energy particles and producing a series of decomposition products of elementary nature. These elements are known as radioactive elements. Uranium, radium, and thorium are examples. The radioactive elements are chemically simple substances, despite their spontaneous decomposition. In 1919, Rutherford and Chadwick caused a change in the chemical nature of nitrogen by subjecting this element to the action of alpha particles, high-energy particles given out by radium. A change by which one elementary substance is converted into one or more other elementary substances is known as transmutation of the element. Many of the elements have been caused to undergo transmutation. The significance the chemist attaches to the name *element* is that elements are simple varieties of matter into which complex substances may be decomposed, and from which complex substances may be formed. There are ninety-two elementary substances. One of these, designated by the number 87, has not yet been obtained either in the elementary condition or in a pure compound. Another element, number 85, has recently been reported in a radioactive form among the disintegration products of radium. One or two additional elements have been reported as products of transmutation processes, but no evidence has been discovered of the existence of these additional elements among natural substances. A list of the elements, together with the symbols used to represent them, appears on the inside front cover of this book. The significance of the atomic

numbers and atomic weights included in this table will be discussed subsequently.

Abundance of the Elements. Only a small number of the elements are plentiful. An estimate of the relative abundance of some elements in the earth's crust, in the oceans, and in the earth, sea, and air together is shown in Table 1, based on data of F. W. Clarke.

TABLE 1. ABUNDANCE OF COMMON ELEMENTS

Name	Per Cent of Earth's Crust	Per Cent of Sea Water	Per Cent of Earth, Sea, Air
Oxygen	46.71	85.79	49.52
Silicon	27.69	——	25.75
Aluminum	8.07	——	7.51
Iron	5.05	——	4.70
Calcium	3.65	0.05	3.39
Sodium	2.75	1.14	2.64
Potassium	2.58	0.04	2.40
Magnesium	2.08	0.14	1.94
Hydrogen	0.14	10.67	0.88
Titanium	0.62	——	0.58
Chlorine	0.045	2.07	0.188
Phosphorus	0.13	——	0.12
	99.515	99.90	99.618

These twelve elements constitute more than 99.5 per cent of the matter in the outer part of the earth and its atmosphere, so that the remaining eighty elements together account for less than $\frac{1}{2}$ per cent. It is interesting to note that many well-known elements, such as carbon and copper, do not appear in the list of the twelve most abundant elements.

The data in the table are based on a very small portion of the entire earth, a layer approximately 10 miles thick. The interior of the earth differs greatly from the outer layer. The specific gravity of the earth is calculated to be 5.522, while that of the outer layer is only 2.79. The crust of the earth is composed primarily of silicate rocks, such as granite. The percentage of silicates decreases and that of iron increases toward the center of the earth.

Compounds. The great majority of the common substances are complex. *Complex substances are compounds.* Compounds have properties that differ from those of the constituent elements. Compounds are characterized by the fact that they have definite composition. Common salt is a compound of sodium with chlorine, known as

sodium chloride. It contains 39.34 per cent of sodium and 60.66 per cent of chlorine. The composition may be determined by a process of *analysis*, which consists in the decomposition of the compound, to find the relative amounts of the constituent elements. The composition may likewise be determined by the process of *synthesis:* *i.e.*, the elements are caused to combine with each other, and the proportions in which they unite are measured. Regardless of the source — whether obtained from sea water, from inland salt lakes, or from salt mines, or produced synthetically in the laboratory — salt always contains these two elements in the same ratio. Analyses of other compounds show that they also contain constant proportions of the component elements. This fact is expressed in the **Law of Definite Composition: The proportions by weight of the elements in each pure compound are fixed and definite.** This law was formulated by Proust in 1802 and was fully confirmed by the accurate experimental work of Stas, about 1860.

The composition of a *mixture* is not definite, but the proportions of the components may be varied at will. Each substance in the mixture is unchanged in composition and retains its own specific properties. Consequently, a mechanical mixture is heterogeneous and has no definite set of properties.

Solutions. When one substance dissolves in another — for example, sugar in water — particles of the dissolved material become uniformly dispersed throughout the solution. These particles cannot be seen and cannot be removed from the solution by filtration. The solution has uniform composition throughout. Nevertheless, the composition of the solution may be varied, and the properties are changed as the composition is altered. The density, freezing point, and boiling point of the solution depend on the proportions and nature of the substances. Although solutions, like compounds, are homogeneous, the properties are not definite but vary according to the composition. Consequently, *solutions are homogeneous mixtures.*

EXERCISES

1. What is a natural science?
2. What factors are involved in the scientific method?
3. What is the significance of experimental data, scientific law, hypothesis, theory?

4. How is the adequacy of a theory determined?
5. What is the field of chemistry?
6. What is the meaning of mass, weight, energy?
7. Name and define the common unit of mass, heat, electrical energy, chemical energy.
8. What is meant by conservation of energy? by the mechanical equivalent of heat?
9. What is a substance? Mention several properties which are used to identify substances.
10. What is the meaning of the terms heterogeneous and homogeneous?
11. What are elements, compounds, solutions?
12. How are compounds distinguished from mechanical mixtures?

SUPPLEMENTARY READINGS

Dampier-Whetham, W. C. D., *A History of Science*, The Macmillan Company, New York, 1930, chaps. I–III.

Moore, F. J., *History of Chemistry*, McGraw-Hill Book Company, Inc., New York, 1939, chaps. I–IV.

French, S. J., *The Drama of Chemistry*, The University Society, Inc., New York, 1937.

Foster, W., *The Romance of Chemistry*, D. Appleton-Century Company, Inc., New York, 1936.

Read, J., *Prelude to Chemistry*, The Macmillan Company, New York, 1937.

Jaffe, B., *Crucibles*, Simon and Schuster, Inc., New York, 1930, secs. I–II.

Gregory, R. A., *Discovery*, The Macmillan Company, New York, 1923.

Findlay, A., *A Hundred Years of Chemistry*, The Macmillan Company, New York, 1937.

Lenard, P. E. A., *Great Men of Science*, translated by H. S. Hatfield, The Macmillan Company, New York, 1933.

Haynes, W., *This Chemical Age*, Alfred A. Knopf, New York, 1942.

Haynes, W., *The Chemical Front*, Alfred A. Knopf, New York, 1943.

Chapter 2

CHANGES IN SUBSTANCES.
THE ATOMIC THEORY

Changes take place continually in natural substances, and many changes are caused by planned experiments. The study of the nature of the changes in matter is an essential part of the science of chemistry. Some of the changes in matter affect the composition of substances, and some do not.

Physical Changes. Liquid water evaporates rapidly when heated in an open vessel, changing into the gaseous state. Gaseous water condenses when cooled, forming liquid water or ice. In cold weather, liquid water freezes into ice, which melts when it absorbs enough heat. Obviously, many of the properties of water are altered during the changes in state. Nevertheless, the compound contains the same proportions of hydrogen and oxygen in each of these states. Solid sugar dissolves in water, losing the crystalline structure characteristic of this solid, but this structure may be recovered by evaporation of the water. Many properties of metals are altered by heating to high temperatures, but are recovered when the metal is cooled to its former temperature. These changes are called physical changes. *A physical change is one in which some of the properties of a substance are altered without changing the composition of the substance.*

Chemical Reactions. Iron rusts when it is exposed to moist air, becoming coated with a red scale. Iron rust is not the simple substance iron in a different physical condition, but is a complex product formed by the metal's reaction with gaseous substances in the air. Metallic magnesium burns when it is heated in air, and the combustion continues, even when the metal is withdrawn from the flame, until all of the sample has burned. The product of this change is a white powder having a series of properties that differentiate it from the metal. Changes of this nature are chemical changes or chemical reactions. *A chemical reaction is a change in which the composition of a substance is altered.* During chemical reactions, there

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is a complete and abrupt change in the properties of the reacting substances because new substances, each possessing its own characteristic properties, are formed.

Chemical reactions are accompanied by definite and specific changes in energy. Reactions in which heat is evolved are *exothermic reactions*, e.g., the combustion of magnesium. Reactions in which heat is absorbed are *endothermic reactions*. The combination of nitrogen with oxygen is an endothermic reaction which is not self-sustaining. Nitrogen does not burn in oxygen.

Magnesium oxide is produced by the reaction of magnesium with oxygen. The compound has a definite composition. Hence, there is only one ratio in which magnesium and oxygen may react to produce this substance, *viz.*, 60.32 parts by weight of magnesium to 39.68 of oxygen. Any excess of either element remains unchanged if quantities in some different ratio are used.

The same relationship applies to all chemical reactions, not merely the union of elementary substances. This generalization is stated as the **Law of Definite Proportions: The proportions by weight of the substances entering into and produced from chemical reactions are fixed and definite.**

The Law of Conservation of Mass. The weight of the magnesium oxide formed by the combustion of magnesium in an atmosphere of oxygen is equal to the sum of the weights of the magnesium and oxygen entering into the reaction. During the burning of coal, however, there appears to be a loss of weight, because the solid residue weighs much less than the coal. The ash represents the incombustible material in coal and the main products are invisible gases. In order to compare the weights of substances involved, the reaction must be carried out in a closed system, or all of the products must be collected and weighed. The significance of this weight relationship may be shown by a simple experiment. Suppose that two solutions containing interreacting substances are placed in opposite limbs of the tube shown in Fig. 2, and that the tube and its contents are counterpoised on a balance. The tube is now removed and tilted so as to mix the solutions and permit reaction. When the tube is replaced on the balance, no change in its weight is observed, even though the substances now have different composition. Repetition of similar experiments with many different

materials leads invariably to the same result. The generalization describing these results was stated by Lavoisier in 1785 as the **Law of Conservation of Mass: The sum of the masses of the substances entering into a chemical reaction is equal to the sum of the masses of the products.** In the combustion of coal, the sum of the weights of coal and oxygen is equal to the sum of the weights of ash and gaseous products.

The laws of conservation of mass and conservation of energy have been verified by a large number of exact measurements.

Fig. 2. Conservation of Mass

Their truth is essential if other quantitative relationships, upon which the foundations of chemistry as an exact science rest, are to have meaning. It is now recognized that a change in mass accompanies a change in energy. The change in mass corresponding to the energy change in chemical reactions is so small that it cannot be detected by weighing the substances. A conservation principle including both matter and energy is rigidly accurate.

Equivalent Weights of Elements. The composition of a compound is commonly stated as the percentage, by weight, of each of the elements it contains. The data expressed on this basis are specific for the particular compound, and no simple relation is apparent between the proportions of the elements in one compound and in another. The following data show the composition of several compounds containing oxygen.
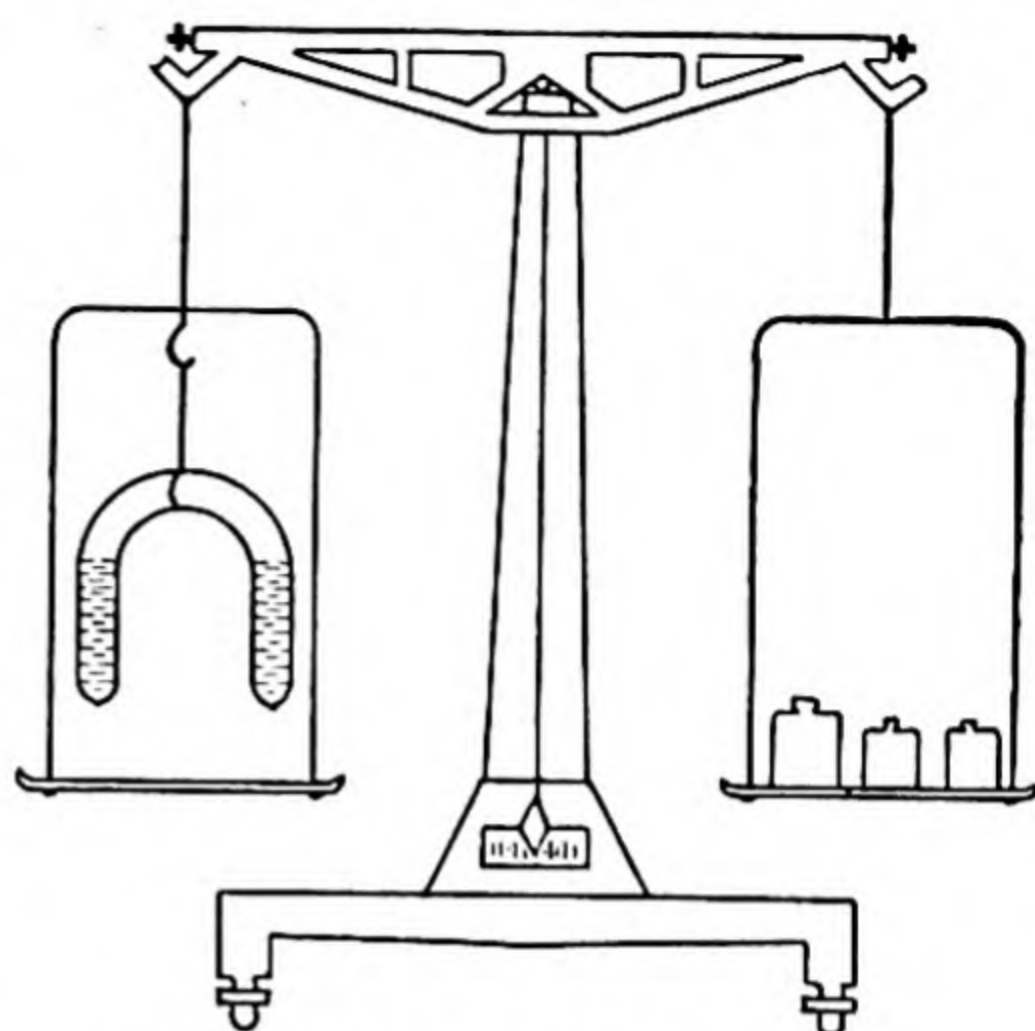
Magnesium Oxide

Magnesium	60.32%
Oxygen	39.68%

Water

Hydrogen	11.18%
Oxygen	88.82%

Aluminum Oxide

Aluminum	52.91%
Oxygen	47.09%

Carbon Dioxide

Carbon	27.27%
Oxygen	72.73%

Chlorine Monoxide

Chlorine	81.57%
Oxygen	18.43%

Phosphorus Pentoxide

Phosphorus	43.68%
Oxygen	56.32%

The composition of these substances may also be expressed as the ratio of the weight of each of the other elements to a specific weight of oxygen. It has been found convenient to select eight parts by weight of oxygen as the basis of this system. Oxygen is chosen because it combines directly with many of the other elements. Eight parts by weight of oxygen is selected because this is the smallest weight that gives a value not less than one for hydrogen.

The calculation of the composition on the oxygen basis from the percentage composition is a simple arithmetical procedure. This may be illustrated by the data for magnesium oxide.

$$\frac{60.32}{39.68} = \frac{X}{8}$$
$$X = 1.52 \times 8 = 12.16$$

The composition of the substances shown above in percentages is expressed on the oxygen basis by the following data

	Magnesium Oxide		*Carbon Dioxide*
Magnesium	12.16	Carbon	3
Oxygen	8	Oxygen	8
	Water		*Chlorine Monoxide*
Hydrogen	1.008	Chlorine	35.46
Oxygen	8	Oxygen	8
	Aluminum Oxide		*Phosphorus Pentoxide*
Aluminum	9	Phosphorus	6.2
Oxygen	8	Oxygen	8

A generalization based on similar data for different compounds may be stated as the **Law of Equivalent Weights: The weights of two substances which are equivalent to the same weight of a third substance are equivalent to each other.** Equivalent, as used in this generalization, means that these quantities have equal value in chemical reactions. Consequently, the numbers showing the weights of the different elements, equivalent to eight parts by weight of oxygen, are called *equivalent weights*. Expressed in grams, they are *gram equivalent weights*. These numbers show a ratio in which the elements combine with each other, or a ratio in which they displace each other. These relations are illustrated in Fig. 3. If an

element forms no compounds with oxygen, a weight equivalent to 8 g. of oxygen may be calculated from the weight which combines with 1.008 g. of hydrogen or 35.46 g. of chlorine. A complete series of equivalent weights may be determined in this manner. Whether any particular pair of elements selected from this list actually combine or not is a specific fact to be learned from experiment. The system of equivalent weights is a direct consequence of the law of definite proportions, not an additional principle.
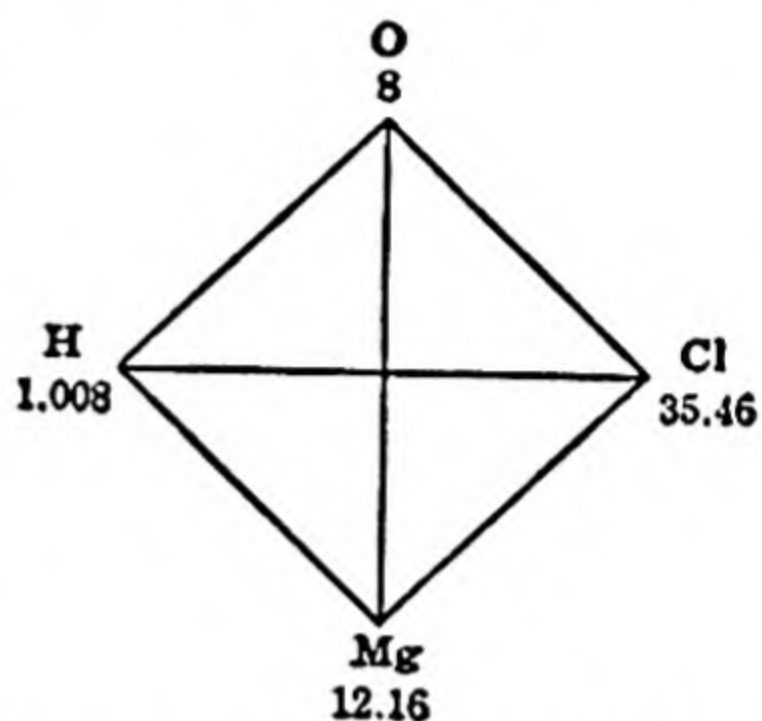
The Law of Multiple Proportions. Many of the elements react with each other in more than one definite ratio, thus forming two or more compounds

Fig. 3. *Equivalent Weights*

containing the same elements. There are two common oxides of carbon, called carbon monoxide and carbon dioxide. The equivalent weight of carbon in the monoxide is 6 and in the dioxide 3. Obviously, the equivalent weight of carbon in the one oxide is double that in the other. In 1803, John Dalton proposed a generalization to describe this relationship, the **Law of Multiple Proportions: Whenever two or more elements yield a series of compounds, the different weights of one element held in combination by a fixed weight of another are in the ratio of small whole numbers.**

The Atomic Theory. At various times in the development of natural science, speculations concerning the nature of matter have involved the notion of an indivisible particle. Leucippus and Democritus in the fifth century B.C., and Leucretius in the first century B.C., set forth this view as part of their general systems of philosophy. Isaac Newton suggested in 1675 that chemical changes result from the separation and the recombination of minute particles. Dalton (1766–1864) is commonly considered to have been the first to deduce scientifically an atomic theory from experimental data. Dalton first advanced his atomic theory in 1803 and published it in his *New System of Chemical Philosophy*, in 1808.

The fundamental assumptions of the atomic theory may be summarized in the following statements.

*All matter is composed of minute particles, atoms, which do not undergo
subdivision during chemical reactions.*

Atoms of the same element have identical properties and mass.

Atoms of different elements have different properties and masses.

*Atoms of different chemical elements combine in simple integral ratios
during chemical reactions.*

The atomic theory affords a satisfactory interpretation of *the law of
conservation of mass* by the assumption that atoms undergo rearrange-
ment during chemical reactions, but are not destroyed. Since no
change in the mass of an atom occurs during chemical reactions,
it follows of necessity that there is no change in the mass of the
system. *The law of definite composition* is fully explained by the theory,
because a given compound always contains the same relative num-
bers of the atoms of the constituent elements. Since each variety of
atom has a characteristic weight, the composition of the com-
pound is dependent on the relative numbers of the atoms and their
weights. *The equivalent weights* of the elements depend on the weights
of the atoms and the numerical ratio in which they react. If the
same two elements yield two different compounds with each
other, it is evident that the numerical ratio of their atoms is differ-
ent in the two compounds. The equivalent weight of carbon in
carbon monoxide is twice its equivalent weight in carbon dioxide.
According to the atomic theory, this means that the number of
atoms of carbon in combination with the same number of atoms
of oxygen is twice as great in carbon monoxide as in carbon dioxide.
Therefore, *the law of multiple proportions* is a logical deduction from
the atomic theory. The verification of the relation stated in this
law gave strong support to the theory.

Modifications in the Atomic Theory. The most important
assumption of the atomic theory is that compounds are formed by
the union of the atoms of the constituent elements in simple integral
ratios. It has now been fully established that atoms are complex
particles which may be decomposed. Nevertheless, the atom is the
chemical unit and it does go through a great variety of chemical
reactions virtually unchanged in mass. It is now known that all of
the atoms of a particular chemical variety do not necessarily have
the same mass, and that many of the elements are composed of

atoms having different masses. These different atoms of one elementary substance have identical chemical properties and are usually present in equal proportions in the natural compounds of the element. Consequently, the average mass of the atoms of an element, determined by experiment, is as definitely fixed as though all of its atoms had precisely the same mass. Although modifications in the statement have followed the discovery of facts that were contradictory to some of its assumptions, the fundamental concepts of the atomic theory are valid. The essential postulates of the atomic theory may be stated as follows: *For each of the elements, there is a reactive unit, the atom, which is characterized by constant average mass.*

The Law of Reacting Volumes. Quantities of gaseous substances are usually measured by volume. The volume of a specific quantity of a substance in the gaseous state varies with the temperature and pressure, as discussed in Chapter 5. Consequently, volumes of gases have quantitative significance only when temperature and pressure conditions are specified. A simple relation exists between the volumes of reacting gases and the volumes of gaseous products when measurements are made under identical temperatures and pressures. Hydrogen and chlorine react with each other in the volume ratio of one to one, and the volume of the gaseous hydrogen chloride formed is double the volume of either the hydrogen or chlorine. The volume ratio in the reaction of hydrogen with oxygen is two to one; in the reaction of hydrogen with nitrogen, three to one. Based on such observations as these, Gay-Lussac in 1808 stated as a generalization the **Law of Combining Volumes of Gases: The volumes of gases taking part in chemical reactions, either as reactants or as products, bear a simple integral ratio to each other if the measurements are made at the same temperature and pressure.**

Avogadro's Hypothesis. The Molecule. In 1811, Avogadro advanced the postulate of the molecule as the physical unit of a substance. *A molecule is the smallest particle of a substance that can exist separated from other like particles, as in the gaseous state or in solution.* Molecules of elementary substances may contain one atom or more than one atom, but all of the atoms in such molecules are of the same chemical variety. Molecules of compounds contain atoms of

two or more varieties. Gay-Lussac's law is satisfactorily explained in terms of **Avogadro's Hypothesis: Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.** The reaction of hydrogen with chlorine involves the same number of molecules of hydrogen and chlorine because the volume ratio is one to one. The number of molecules of hydrogen chloride formed is double the number of molecules of hydrogen and also double the number of molecules of chlorine because the volume is twice as great. Each molecule of hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Hence, it is necessary to conclude that the molecules of both hydrogen and chlorine contain two atoms, because two atoms are obtained from each of these molecules during the reaction. Similar reasoning based on the volume ratio in the reaction of hydrogen with oxygen leads to the conclusion that the molecules of oxygen are diatomic.

Atomic Weights. The weights of the atoms of the elements expressed in grams are such small numbers that a different unit is required to give numbers of convenient magnitude. The choice of this unit is arbitrary. At one time, the weight of the hydrogen atom was selected as the unit. Subsequently, it became apparent that certain advantages were gained by basing the unit on oxygen with an atomic weight of 16. This gives a value of 1.008 for the hydrogen atom, the lightest of the atoms. *The atomic weight is the average weight of the atoms of an element in atomic weight units, each equal to one sixteenth of the weight of the oxygen atom.* The atomic weights of most elements are nearer to whole numbers on this basis than if calculated in hydrogen units.

The atomic weights shown in the Table of Atomic Weights on the inside front cover of this book have been determined experimentally. The determination of the atomic weight of an element is based on two important relationships, *viz.*, the atoms are the reacting unit particles of the elements, and the equivalent weights express a weight ratio in which the elements react. Consequently, the atomic weight is a multiple of the equivalent weight. The value of this multiple depends on the numerical ratio in which the atoms react. Experimental methods for the determination of the atomic weights are discussed in Chapter 9.

Molecular Weights. Since molecules are composed of atoms, the atomic weight unit is satisfactory for measuring molecular weights. *The molecular weight is the weight of one molecule of a substance in atomic weight units.* The weight of a molecule is necessarily equal to the sum of the weights of all the atoms it contains. Direct methods for weighing single molecules are not available, but it is possible to determine experimentally the weights of the same number of molecules of two substances. One method of doing this is to weigh equal volumes of two gases under the same conditions of temperature and pressure. The weights of the same number of molecules of two substances are in the same ratio as the weights of the individual molecules. The numbers obtained in this manner are, therefore, reduced to the arbitrary basis on which the atomic weight of oxygen is 16.

The Gram Atom and the Mole. Although atoms and molecules are the chemical and physical units, respectively, of substances, much larger quantities of materials are used in all experimental procedures. Consequently, it is desirable to convert atomic and molecular weights to the ordinary units of weight, while still retaining their significance as relative weights. This may be accomplished by multiplying atomic and molecular weights by one gram, since the validity of a ratio is not altered by multiplying both members by the same term. *The weight in grams which is numerically equal to the atomic weight of an element is one gram atom, and the weight in grams numerically equal to the molecular weight of a substance is one gram molecule or one mole.* The atomic weight of oxygen is 16 and one gram atom is 16 g. One mole of water is 18.016 g. and one mole of carbon dioxide is 44 g. Gram molecules of two different substances contain the same number of molecules of each, because these quantities are in the same ratio as the weights of the individual molecules. The actual number of atoms in one gram atom of any element is very large,* 6.064×10^{23}. This is also the number of molecules in one mole, and is commonly called the Avogadro Number. The gram atom of an element is the weight in grams of 6.064×10^{23} atoms of the element and the mole is the weight in grams of 6.064×10^{23} molecules of the substance.

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* Large numbers are conveniently expressed as a power of the base 10. For the significance of these numbers, see Appendix XIV.

Symbols. The elements are represented by a special notation employing symbols. The symbol of an element is the first letter in its name, or the first letter followed by some other distinguishing letter if there are two or more elements whose names have the same initial letter. Thus, C is the symbol for carbon; Ca, calcium; Cl, chlorine; Co, cobalt; and Cr, chromium. Some of the symbols are derived from the Latin names, *e.g.*, Cu, cuprum, copper; Au, aurum, gold; Fe, ferrum, iron; and Pb, plumbum, lead. The symbol is not merely an abbreviation for the name of the element. It also has quantitative significance. Thus, the symbol Cl represents the element chlorine, and it also represents one atom, one atomic weight, and one gram atom of this element.

Formulas. The molecules of substances are represented by formulas. Formulas are written by the use of the symbols of the elements, followed by subscript numbers showing the number of atoms of each element in one molecule, if this number is greater than one. The oxygen molecule contains two atoms and its formula is O_2. Similarly, molecular hydrogen is diatomic and has the formula H_2; nitrogen, N_2; and chlorine, Cl_2. Solid elementary substances are commonly represented by the symbol. Thus, elementary carbon is represented by C. The formulas of compounds include the symbols of all of the elements they contain, with subscripts as noted above. Carbon monoxide contains the elements carbon and oxygen in the atomic ratio of one to one, CO. The molecule of carbon dioxide contains one atom of carbon and two of oxygen, CO_2. The formula of sulfuric acid is H_2SO_4. A number of compounds contain groups of atoms which act as units in a series of reactions, but do not exist as independent molecular particles. Such groups are known as *compound radicals*. Radicals are treated as individual particles in writing formulas of compounds. A number of compounds contain the hydroxide radical, composed of one atom each of hydrogen and oxygen, *e.g.*, sodium hydroxide, NaOH; calcium hydroxide, $Ca(OH)_2$; and aluminum hydroxide, $Al(OH)_3$. The subscript outside of the parenthesis refers to all of the atoms included. The sulfate radical, composed of one atom of sulfur and four of oxygen, appears in many compounds, *e.g.*, sodium sulfate, Na_2SO_4; calcium sulfate, $CaSO_4$; and aluminum sulfate, $Al_2(SO_4)_3$.

Each symbol retains its complete significance when written in

a formula, and formulas represent the composition of substances. The formula also represents a definite weight, one mole of the substance. The formula H_2SO_4 states the fact that the compound, sulfuric acid, is composed of elements in the ratio of two atoms of hydrogen to one atom of sulfur and four atoms of oxygen. The molecular weight of sulfuric acid is 98.076, the sum of two atomic weights of hydrogen, 2×1.008, one atomic weight of sulfur, 32.06, and four atomic weights of oxygen, 4×16. One mole of sulfuric acid is 98.076 g. Even though molecules may not exist as distinct physical particles, as in many crystalline solids, formulas are employed to represent composition. The formula of sodium chloride, NaCl, shows that one mole of this salt, 58.46 g., contains one gram atom of sodium, 23 g., and one gram atom of chlorine, 35.46 g.

Percentage Composition from the Formula. The per cent of each element in a compound may be calculated if the formula is known. The percentages of the elements in sulfuric acid, H_2SO_4, — discussed in the preceding paragraph — are:

$$\frac{2.016}{98.076} \times 100 = 2.05 \text{ per cent of hydrogen}$$

$$\frac{32.06}{98.076} \times 100 = 32.70 \text{ per cent of sulfur}$$

$$\frac{64.0}{98.076} \times 100 = 65.25 \text{ per cent of oxygen}$$

Formulas from Percentage Composition. In order to derive a formula from the percentage composition, it is necessary to calculate the atomic ratio from the weight ratio. The atomic ratio is calculated by finding the number of gram atoms of each element in the quantities shown by the weight ratio. The gram atom ratio is then reduced to the simplest integral ratio. An oxide of sulfur contains 50 per cent each of oxygen and sulfur, i.e., 100 g. of the oxide contain 50 g. of oxygen and 50 g. of sulfur. These weights are divided by the gram atomic weights to obtain the atomic weight ratio.

$$50 \text{ g.} \div 16 \text{ g.} = 3.12 \text{ gram atoms of oxygen}$$
$$50 \text{ g.} \div 32 \text{ g.} = 1.56 \text{ gram atoms of sulfur}$$

These numbers of gram atoms show that there are twice as many atoms of oxygen as of sulfur in the compound, because the simplest

ratio is one to two. Hence the simplest formula, known as the *empirical formula*, is SO_2. Both members of this ratio may be multiplied by the same number without destroying the validity of the ratio. Therefore, the formulas, S_2O_4, S_3O_6, S_4O_8, S_xO_{2x}, express the same weight ratio as the simple formula, SO_2. To determine the true formula from the empirical formula, the molecular weight of the compound must also be determined. Suppose that experimental determination shows molecular weight of this oxide to be about 64. This weight is sufficiently accurate to show that the true formula is SO_2 — which has an actual molecular weight of 64 $(32 + 2 \times 16)$ — for the formula, S_2O_4, demands a molecular weight of 128.

It is found by experiment that the equivalent weight of aluminum is 9. This means that 9 g. of aluminum combine with 8 g. of oxygen. The atomic weight ratio of these elements in their oxide is calculated in the following manner:

$$9 \text{ g.} \div 27 \text{ g.} = 0.333 \text{ gram atom of aluminum}$$
$$8 \text{ g.} \div 16 \text{ g.} = 0.5 \text{ gram atom of oxygen}$$

Dividing these numbers of gram atoms by the smallest, it is found that there are 1.5 gram atoms of oxygen for 1 gram atom of aluminum. The simplest integral ratio, consequently, is two atoms of aluminum to three of oxygen; and the empirical formula is Al_2O_3. The same procedure is followed in deriving the formula of a compound containing more than two elements. It is found by experiment that 10 g. of a certain compound contain 2.91 g. of sodium, 4.05 g. of sulfur, and 3.04 g. of oxygen. First, the number of gram atoms in the specified weight of each element is calculated.

$$2.91 \text{ g.} \div 23 \text{ g.} = 0.126 \text{ gram atom of sodium}$$
$$4.05 \text{ g.} \div 32 \text{ g.} = 0.126 \text{ gram atom of sulfur}$$
$$3.04 \text{ g.} \div 16 \text{ g.} = 0.19 \text{ gram atom of oxygen}$$

These numbers of gram atoms are then reduced to the simplest integral ratio.

Na	S	O
0.126 | 0.126	0.126 | 0.126	0.126 | 0.19
1	1	1.5

From this it is clear that the simplest integral ratio is 2 : 2 : 3, and the formula is $Na_2S_2O_3$.

Valence. The formulas of several hydrogen compounds, derived by the method discussed in the preceding paragraph, are found to be HCl, H_2O, NH_3, and CH_4, i.e., one atom of chlorine combines with one atom of hydrogen, one of oxygen with two of hydrogen, one of nitrogen with three of hydrogen, and one of carbon with four of hydrogen. The capacity of these atoms for combination with hydrogen atoms are in the order of the numbers 1, 2, 3, and 4. Similarly, the formulas of a series of chlorine compounds are found to be $NaCl$, $CaCl_2$, $AlCl_3$, CCl_4, and PCl_5, i.e., the capacity of these elements for holding chlorine atoms in combination is shown by the numbers 1, 2, 3, 4, and 5, respectively. A system may be devised in which numbers are assigned to different elements representing their combining capacities. The unit for this system of numbers is the hydrogen atom, because no other atom exhibits a smaller combining value. Elements whose atoms combine with or replace two atoms of hydrogen are assigned the number 2; those whose atoms combine with or replace three atoms of hydrogen are given the number 3; and so on through the list. These numbers are called valences. *The valence of an element is equal to the number of atoms of hydrogen which one atom of this element may combine with or replace.* The valence of an element which yields no hydrogen compounds, and which does not displace hydrogen directly, is found by comparison with some third element. Elements which exhibit valence 1 are frequently called monovalent; those having valence 2, divalent; 3, trivalent; and 4, tetravalent.

The valences of some elements are considered to be positive and others to be negative. Experimental evidence shows that in many instances these numbers and signs represent electrical charges, but that in others the distinction is more or less arbitrary. The significance of the positive and negative nature of valence is discussed in Chapter 13. The valences of some of the common elements and radicals are shown in Table 2. Some elements have more than one valence, a natural consequence of the fact that in many instances the same two elements may yield two or more compounds. A more inclusive list appears in Tables III and IV in the Appendix.

TABLE 2. VALENCES OF COMMON ELEMENTS AND RADICALS

1 +	2 +	3 +	1 −	2 −	3 −
H	Mg	Al	Cl	S	PO$_4$
Na	Ca	Fe	Br	SO$_3$	
K	Zn		I	SO$_4$	
Hg	Cu		OH	CO$_3$	
Ag	Hg		NO$_3$	O	
	Fe				

Formula Writing. The formulas of compounds indicate the relative numbers of the atoms of the component elements. The relative numbers of atoms must be in a ratio that gives an equal number of positive and negative valence units. The valence of hydrogen is 1 + and of chlorine 1 −, and the formula of hydrogen chloride is HCl. The valence of zinc is 2 + and of sulfur in sulfides 2 −. Hence, the formula of zinc sulfide is ZnS. Elements with valences of the same number but opposite sign combine with each other in the atomic ratio of one to one if at all. If the numerical values of the valences are different, the correct ratio is estimated through the use of the lowest common multiple. The valence of aluminum is 3 + and of oxygen 2 −. The least common multiple of these numbers is 6. Therefore, the atomic ratio of these elements in the oxide is two of aluminum to three of oxygen and the formula is Al_2O_3. The oxide of phosphorus having a valence of 5 + is P_2O_5. The valences of compound radicals are treated in the same manner as those of atoms. The sulfate radical has a valence of 2 −, and the formula of aluminum sulfate is $Al_2(SO_4)_3$.

In order to write correct formulas it is necessary to know the elements present in the compound and the valence of each element in the substance. Formulas represent the composition of substances and have no meaning unless the substances actually exist.

Equations to Represent Chemical Reactions. Chemical reactions are commonly represented by equations. Writing equations consists in placing the formulas of the initial substances to the left and the formulas of the products to the right of the reaction symbol, usually shown as an arrow ($\longrightarrow$). Next, the correct proportions must be shown by balancing the equation, *i.e.*, by writing coefficients before the formulas to show the correct ratio. The same

total number of atoms of each of the elements must be shown in the initial substances and in the products. Equations do not show the total number of molecules involved in the reaction, but they do show the molecular ratio. The correctness of an equation may be judged by the following considerations: first, it represents an experimental fact; second, the formulas show the composition of the substances; third, the equation is balanced so that the proportions expressed by the formulas are correct.

The reaction of magnesium with oxygen may be selected as a simple example to illustrate the method of deriving equations. The experimental fact is that these elements do unite to form magnesium oxide. Elementary magnesium is represented by the symbol Mg, oxygen by the formula O_2, and magnesium oxide by the formula MgO. The first step in writing the equation is shown by the expression:

$$Mg + O_2 \longrightarrow MgO$$
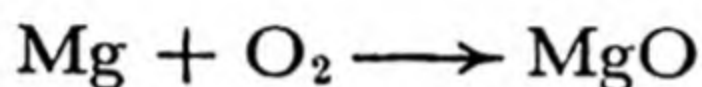
This is not an equation because it does not show the correct proportions of the substances. Two atomic weights of oxygen are represented by O_2, but only one, by MgO. Hence, two molecular weights of magnesium oxide must be shown. This is done by the use of the coefficient 2 with MgO to give 2 MgO. This balances the expression as far as oxygen is concerned, but not magnesium. Two atomic weights of magnesium are required to produce two molecular weights of magnesium oxide. Consequently, the coefficient 2 is written before the symbol Mg, giving 2 Mg. The complete equation is

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$
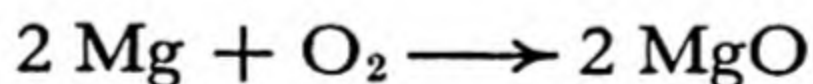
Calculation of Reacting Quantities of Substances. Equations show the proportions in which the substances react. Consequently, the quantity of one of the substances involved establishes the quantities of all of the others. In the equation the proportions of the reacting substances are expressed in moles and gram atoms. The quantities in other units of measurement are calculated by converting the ratio in moles and gram atoms to these other units. The calculations require the simple arithmetical steps of addition, subtraction, multiplication, and division. From the equation,

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$
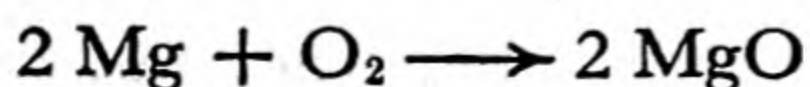
derived in the preceding paragraph, it is observed that 2 gram atoms of magnesium react with 1 mole of oxygen to form 2 moles of magnesium oxide. It is found by reference to the table of atomic weights that the atomic weight of magnesium is 24.32 and of oxygen, 16. The equation, therefore, states the fact that 48.64 g. of magnesium require 32 g. of oxygen for complete combustion and that 80.64 g. of magnesium oxide are formed. The weight of oxygen required to react with a specified weight of magnesium, 5 g. for example, bears the same ratio to a mole of oxygen that 5 g. bears to 2 gram atoms of magnesium.

$$\frac{X \text{ g. of oxygen}}{1 \text{ mole of oxygen}} = \frac{5 \text{ g. of magnesium}}{2 \text{ gram atoms of magnesium}}$$

$$\frac{X \text{ g.}}{32 \text{ g.}} = \frac{5 \text{ g.}}{48.32 \text{ g.}}$$

$$X = \frac{5}{48.64} \times 32 = 0.1028 \times 32 = 3.29 \text{ g. of oxygen}$$

The weight of magnesium oxide formed in this reaction is calculated in the same manner.

$$\frac{X \text{ g.}}{80.64 \text{ g.}} = \frac{5 \text{ g.}}{48.64 \text{ g.}}$$

$$X = 0.1028 \times 80.64 \text{ g.} = 8.29 \text{ g. of magnesium oxide}$$

The quantities of gases are usually expressed in volumes, measured under specified conditions of temperature and pressure. Equal volumes of all gases at the same temperature and pressure contain the same number of molecules, according to Avogadro's hypothesis. Since one mole of all gases contains the same number of molecules, the volume of one mole is the same for all gases at the same temperature and pressure. The volume of one mole of any gas at 0° and 760 mm. is found by experiment to be approximately 22.4 liters. The volume of oxygen at 0° and 760 mm. required for the reaction with 5 g. of magnesium may be calculated directly from the equation by using 22.4 liters as the measure of one mole of oxygen.

$$\frac{X \text{ liters}}{22.4 \text{ liters}} = \frac{5 \text{ g.}}{48.64 \text{ g.}}$$

$$X = 0.1028 \times 22.4 \text{ liters} = 2.30 \text{ liters of oxygen}$$

The applications of these principles will be illustrated in subsequent sections in connection with other reactions.

EXERCISES

1. What is the essential difference between physical and chemical changes?
2. What is a chemical reaction? What three effects characterize chemical reactions?
3. State, and cite examples to illustrate, the laws of definite proportions and conservation of mass.
4. What is meant by the equivalent weight of an element? State and explain the meaning of the law of equivalent weights.
5. State the important postulates of Dalton's atomic theory, and show how the weight relationships observed in chemical reactions are explained in terms of this theory.
6. State the law of combining volumes of gases, and show how this law leads to the supposition known as Avogadro's hypothesis.
7. What is the atomic weight of an element? Explain the fact that the atomic weight is a multiple of the equivalent weight if the two weights are not the same.
8. Define: atom, molecule, gram atom, mole.
9. State the complete significance of the symbol of an element and of the formula of a compound.
10. Explain the steps involved in calculating the formula of a substance from the percentages of the component elements.
11. What is meant by the valence of an element? Show how the valences of the elements and radicals are applied in writing formulas.
12. Outline the experimental proof that molecular oxygen is diatomic.
13. State in words the facts expressed in the equation for the reaction of magnesium with oxygen.
14. Apply these facts by calculating the weight of magnesium and the weight and volume of oxygen required to produce: (a) 0.5 moles of magnesium oxide; (b) 5 moles of magnesium oxide; (c) 2.5 g. of magnesium oxide.

SUPPLEMENTARY READINGS

Dampier-Whetham, W. C. D., *A History of Science*, The Macmillan Company, New York, 1930, chap. IV.

Moore, F. J., *History of Chemistry*, McGraw-Hill Book Company, Inc., New York, 1939, chaps. VII–VIII.

Jaffe, B., *Crucibles*, Simon and Schuster, Inc., New York, 1930, secs. VII–VIII.

Gregory, J. C., *A Short History of Atomism*, A. & C. Black, Ltd., London, 1931.

Findlay, A., *A Hundred Years of Chemistry*, The Macmillan Company, New York, 1937.

Holmyard, E. J., *Chemistry to the Time of Dalton*, The Oxford University Press, Oxford, 1925.

Dalton, J., "Foundations of the Atomic Theory," *Alembic Club Reprints No. 2*, Oliver and Boyd, Edinburgh, 1923.

Dalton, J., "Foundations of the Molecular Theory," *Alembic Club Reprints No. 4*, Oliver and Boyd, Edinburgh, 1923.

Coward, H. F., "John Dalton," *J. Chem. Education* **4**, 22 (1927).

Atkinson, E. R., "The Atomic Hypothesis of William Higgins," *J. Chem. Education* **17**, 3 (1940).

Chapter 3

OXYGEN. THE ATMOSPHERE

Oxygen, the most abundant of the elements, occurs as an important component of the atmosphere. Consequently, many of the properties and reactions of this element are widely known from casual observation. Reactions of oxygen in the burning of common fuels furnish a large portion of the energy required for heating our homes, cooking our food, and performing a vast number of industrial operations. Oxygen, absorbed from the air in respiration, is essential to life. The chemistry of oxygen serves as an introduction to one of the simple types of chemical reactions, the combination or direct union of elements.

Historical Background. The correct interpretation of the behavior of oxygen marks an important step in the development of chemistry as a science. In the year 700, Chinese scientists understood that air is composed of at least two materials and that only one of these is active, *i.e.*, causes changes in certain materials in contact with it. Mayow, in 1669, recognized the presence of an active gas in air and its role in combustion. His views were not generally accepted, and the phenomena accompanying combustion were interpreted in terms of a theory advanced by Becher in 1669 and further developed by Stahl about 1702. According to this theory, the hypothetical substance "phlogiston" emerges from the burning materials and gives rise to the heat and light which are observed. It was assumed that air must be present to absorb the phlogiston as it emerges. The fact that in many instances the products of combustion weigh more than the original materials either was not noticed or was ignored as of little significance. This theory was widely accepted and it persisted for many years.

Scheele, a Swedish apothecary, prepared oxygen from several substances in 1771–1772, and recognized it as the active component of air, but his work was not published until 1777. In the

meantime, Priestley, an English clergyman who spent a great deal of his time on scientific experiments, became interested in studying the effect of heating different substances and examining any gaseous products. In 1774, he heated mercuric oxide and observed the formation of a gas. This gas caused a candle to burn more brilliantly than in air. But Priestley did not recognize this gas as a component of air, and he thought it caused substances to burn more brilliantly than air because it was a better absorbent for phlogiston. So he called the gas "dephlogisticated air." Nevertheless, Priestley is commonly credited with the discovery of oxygen.

In 1777, Lavoisier established clearly the nature of changes during the rusting of metals. A quantity of mercury was heated in a retort arranged so that the open end projected into a jar of air enclosed over water, as in Fig. 4. When no further contraction in the volume of the air could be observed, it was found that the volume of the remaining gas was four fifths of the original volume. The residual gas did not support combustion. A red solid, which had formed on the surface
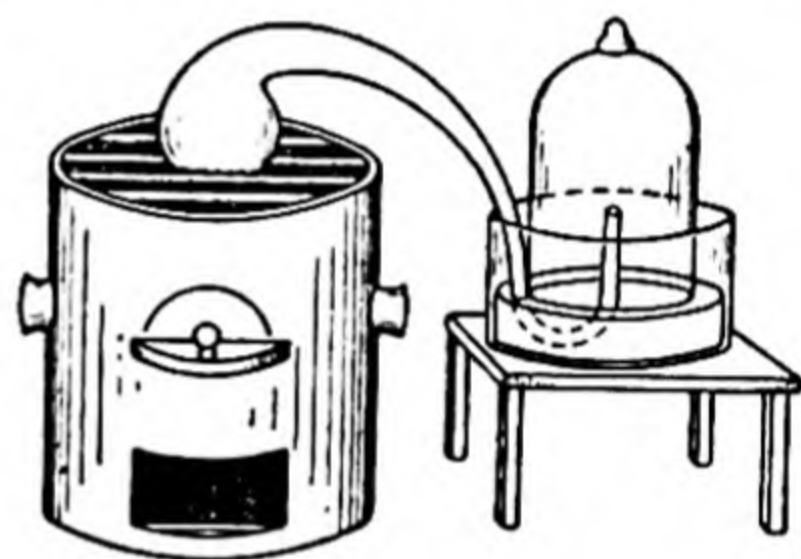
Fig. 4. Lavoisier's Experiment

of the mercury during the period of heating, was then heated more intensely in a small retort with the formation of free mercury and a gas. The volume of this gas was found to be equal to the contraction noted during the formation of the red solid. Moreover, this gas showed to a high degree all of the active properties lost by the air during the period of heating in contact with mercury. It thus was proved that the gas prepared by Priestley is the active component of air, and that rusting is due to the combination of this substance with the metal. Lavoisier named the gas oxygen in the mistaken belief that it was an essential constituent of all acids. On the basis of the described experiment, the correct interpretation of the role of oxygen in combustion and respiration was established, and the phlogiston theory and other notions about the material nature of fire were proven false.

Occurrence of Oxygen. Approximately one half of the matter in the outer crust of the solid earth, the seas, and the air is oxygen. The element occurs in uncombined condition in air which

is one fifth by volume and nearly one fourth by weight oxygen. The other main component of the air is nitrogen. Oxygen occurs extensively in compounds also. Water is about 89 per cent oxygen, the bodies of animals are approximately 60 per cent, the common rocks 45–50 per cent.

Preparation of Oxygen. The properties of oxygen are affected by the presence of the other gases in the air. Consequently, to investigate its properties accurately, samples of pure gas must be procured. There are many uses of oxygen that require the substance in a high degree of purity so as to eliminate the effect of the presence of other gases. The method selected for the preparation of any substance depends on several factors such as the availability of raw materials, the quantity of the substance required, the degree of purity demanded, and the cost of the procedure. Usually, large quantity production is an important industrial consideration, and the cost must be low enough to permit successful competition with products obtained by other methods. Only a small sample of a substance is required for study in the laboratory, so that usually cost is not a deciding factor in the selection of the method. The purity of the product and the simplicity of the procedure are the important considerations.

Industrial Preparation of Oxygen. The most important industrial source of oxygen is the air. Air may be converted into a liquid by cooling it sufficiently. Carbon dioxide, water vapor, and dust are separated before liquefaction, and the liquid product is a solution of the other atmospheric substances in each other. When liquid air boils, nitrogen escapes from the solution more rapidly than oxygen, because its boiling point, − 195.8°, is lower than that of oxygen, − 183°. By the use of the proper devices, most of the nitrogen may be boiled out without much oxygen escaping. The oxygen boiled from the liquid, having a purity of 96–99 per cent, is compressed into steel cylinders under a pressure of 2000 lb. per square inch.

Another way of preparing oxygen industrially is by passage of a direct current of electricity through water. For this purpose, water containing a small proportion of sodium hydroxide or sulfuric acid — to serve as a conducting medium — is employed. Water is decomposed with the liberation of oxygen at the positive

electrode, the anode, and hydrogen at the negative electrode, the cathode. The gases are collected separately, dried, and stored under pressure in cylinders.

Laboratory Preparation of Oxygen. Neither of the industrial methods for the preparation of oxygen is ordinarily used in the laboratory. No naturally occurring materials, except air and water, are suitable for direct use in the preparation of oxygen. Consequently, the laboratory method involves the decomposition of compounds, which have themselves been prepared from natural substances. Scheele, Priestley, and Lavoisier obtained small samples of oxygen by heating mercuric oxide. Since the valence of mercury in this compound is 2 +, the formula of the oxide is HgO. The equation for the decomposition reaction is:

$$2\,HgO \longrightarrow 2\,Hg + O_2$$
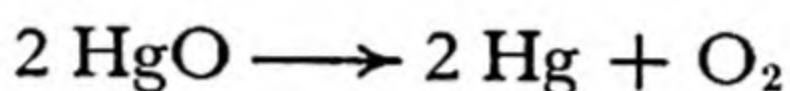
Several other oxides may be decomposed by heat, yielding either all or a portion of the oxygen they contain. Among these are silver oxide, Ag_2O, manganese dioxide, MnO_2, and lead dioxide, PbO_2. But most of the metal oxides cannot be decomposed except at high temperatures.

The nitrates of sodium and potassium may be decomposed by heat to release one third of the oxygen content and to form the nitrite. Both the nitrate radical and the nitrite radical have a valence of 1 −. The formulas of these sodium compounds are $NaNO_3$ and $NaNO_2$, respectively, and the equation for the reaction that produces oxygen is:

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2$$
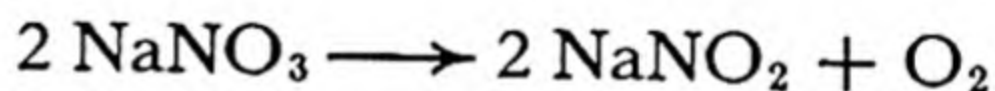
Another convenient method for the preparation of limited quantities of oxygen is based on the reaction of water with sodium peroxide. The products of this reaction are sodium hydroxide and oxygen. The valence of the peroxide radical is 2 − and of the hydroxide radical 1 −. The sodium compounds are represented by the formulas Na_2O_2 and $NaOH$, respectively. The equation for the reaction is:

$$2\,H_2O + 2\,Na_2O_2 \longrightarrow 4\,NaOH + O_2$$
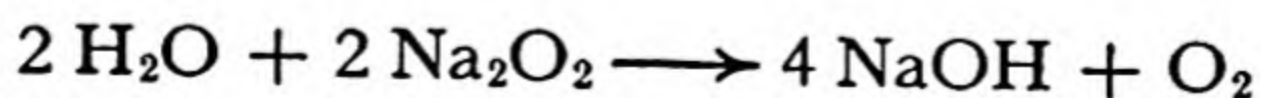
The most generally used laboratory method for the preparation of oxygen is based on the thermal decomposition of potassium

chlorate. This substance contains 31.9 per cent of potassium, 28.93 per cent of chlorine, and 39.17 per cent of oxygen. It is represented by the formula $KClO_3$. It melts at 368° and begins to decompose with the evolution of oxygen at a noticeable rate, at about 400°.

$$2 KClO_3 \longrightarrow 2 KCl + 3 O_2$$
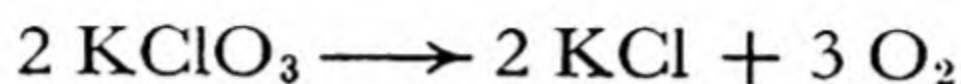
The velocity of this reaction is greatly increased by the presence of a small proportion of manganese dioxide or ferric oxide. In the presence of manganese dioxide it is necessary to heat the material to only around 200° to cause evolution of oxygen at a suitable rate. At this temperature, oxygen is released exclusively by the potassium chlorate, and manganese dioxide remains unaltered at the end of the experiment. Manganese dioxide serves as a catalyst in this reaction. *A catalyst is a substance which alters the velocity of a reaction but remains unchanged in composition at the end of the reaction.*

In laboratory practice, a mixture of potassium chlorate and manganese dioxide is heated just enough to cause the evolution of oxygen at a convenient rate. The gas is collected by the displacement of water in an inverted bottle full of water. (Fig. 5.) This method is suitable for the collection of gases of low solubility.
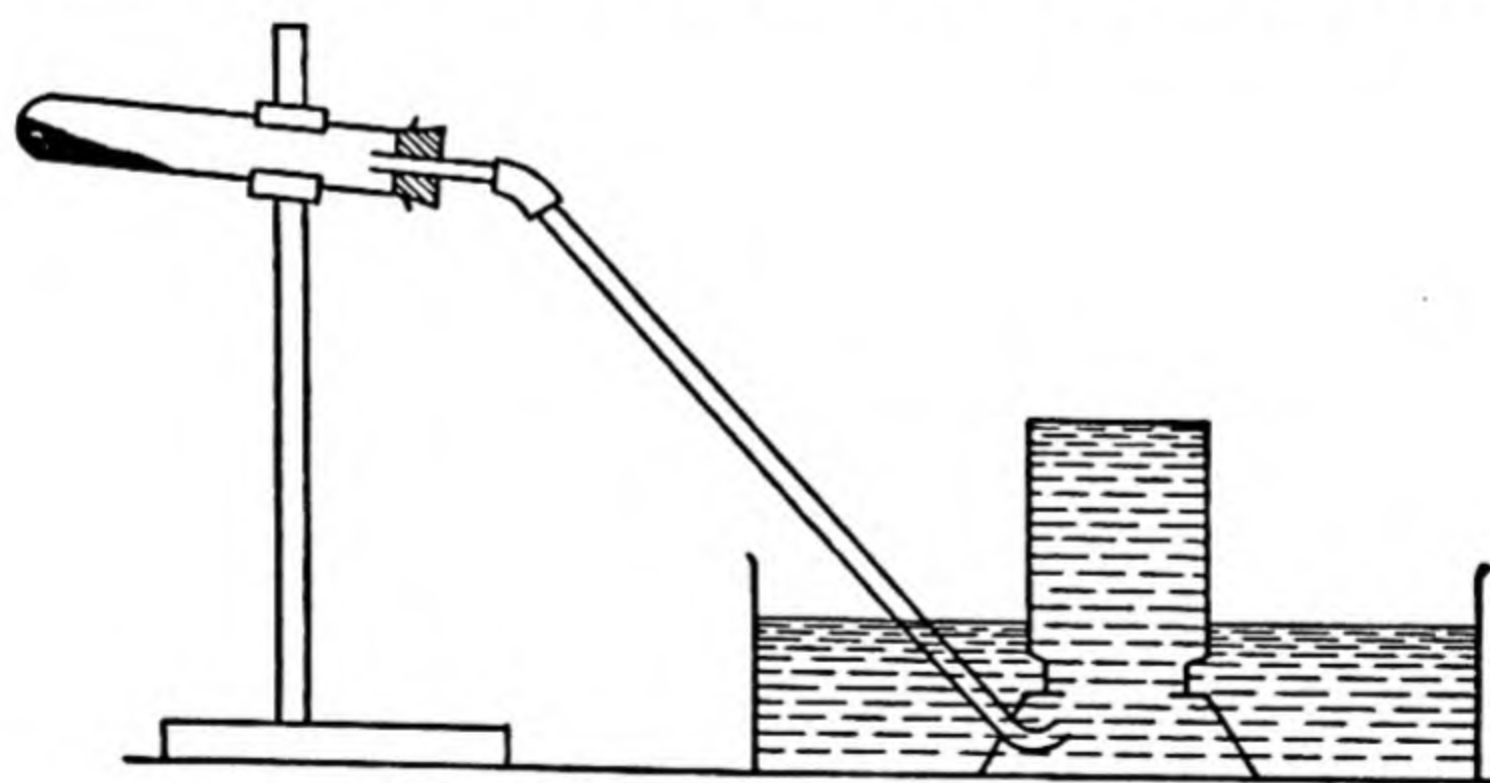
Fig. 5. Production of Oxygen

The quantity of oxygen obtainable from a specified weight of potassium chlorate, *e.g.*, 10 g., may be calculated as illustrated in the examples in the last section of the preceding chapter. From the equation, it is observed that 2 moles of potassium chlorate yield 3 moles of oxygen. These quantities in grams are 245.12 g. of potassium chlorate and 96 g. of oxygen.

$$\frac{X \text{ g. of oxygen}}{96 \text{ g. of oxygen}} = \frac{10 \text{ g. of potassium chlorate}}{245.12 \text{ g. of potassium chlorate}}$$

$$X = \frac{10}{245.12} \times 96 = 0.0408 \times 96 = 3.917 \text{ g. of oxygen}$$

The volume of dry oxygen, measured at 0° and 760 mm., may also be calculated from the equation.

$$\frac{X \text{ liters}}{3 \times 22.4 \text{ liters}} = \frac{10 \text{ g.}}{245.12 \text{ g.}}$$

$$X = 0.0408 \times 67.2 = 2.74 \text{ liters of oxygen}$$

Properties of Oxygen. At ordinary temperatures oxygen is a colorless, odorless, and tasteless gas. One liter of oxygen, at 0° and 760 mm., weighs 1.429 g. One liter of air under these conditions weighs 1.273 g., so that oxygen is 1.12 times as dense as air. The gas is slightly soluble in water, approximately 3 volumes of oxygen in 100 volumes of water, at 20° and 760 mm., 4.9 volumes, at 0° and 760 mm. The gas may be liquefied at low temperatures and high pressures, but the highest temperature at which liquefaction may occur is − 118.8°. This temperature is known as the critical temperature. *The critical temperature is the highest temperature at which the liquid and gaseous phases of a substance may exist together in a stable mixture.* The pressure of the gas at the critical temperature is known as the *critical pressure.* This pressure for oxygen is 48.7 times normal atmospheric pressure. Liquid oxygen has a pale blue color. Its boiling point is − 183° and its freezing point − 218.4°.

Reactions of Oxygen. Substances burn more rapidly in an atmosphere of oxygen than in air. A test for the presence of oxygen in high proportions is based on the fact that a glowing splinter is ignited when it is inserted into a jar of the gas. Most oxygen reactions occur rather slowly at room temperatures. Many substances which react vigorously with oxygen at high temperatures remain virtually unchanged in an atmosphere of oxygen at ordinary temperatures.

Reactions with Elementary Substances. Hydrogen burns rapidly when a stream of the gas is ignited in an atmosphere of oxygen, and mixtures of the two gases explode. Water, the oxide of hydrogen, is the product of this reaction.

$$2 H_2 + O_2 \longrightarrow 2 H_2O$$
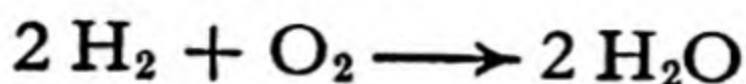
Metallic calcium burns vigorously when it is ignited in an atmosphere of oxygen, forming the white solid, calcium oxide, CaO.

$$2\,Ca + O_2 \longrightarrow 2\,CaO$$
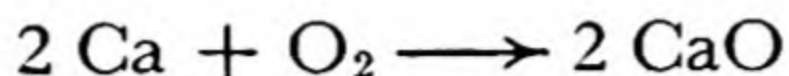
Phosphorus burns vigorously in air, forming a white smoke consisting of finely divided solid particles of an oxide of phosphorus, known as phosphorus pentoxide, P_2O_5. In an atmosphere of pure oxygen, the rate of reaction is so great that a blinding white light is emitted.

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5$$
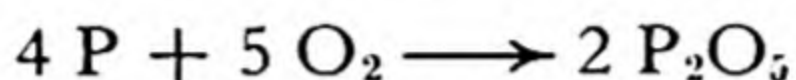
All the common elements unite directly with oxygen except three groups, *viz.*, the inert gases of the helium family, helium, neon, argon, krypton, xenon, and radon; the noble metals, silver, gold, and the platinum metals; and the halogens, fluorine, chlorine, bromine, and iodine. Except for the inert gases, compounds of all elements with oxygen are known.

Products of the reaction of oxygen with other elements are called oxides. The suffix *-ide* usually denotes a binary compound, a compound containing two elements only. There are two plans for distinguishing the oxides of elements which form two compounds with oxygen. One plan involves the use of the prefixes, *mono-*, *di-*, *tri-*, *tetra-*, etc., with the word oxide to indicate the number of atoms of oxygen in one molecule of the compound. The following names and formulas illustrate the use of this system: carbon monoxide, CO; carbon dioxide, CO_2; sulfur dioxide, SO_2; sulfur trioxide, SO_3; phosphorus trioxide, P_2O_3; phosphorus pentoxide, P_2O_5. The other plan involves the use of the suffixes *-ous* and *-ic* with a significant part of the name of the element combined with oxygen. The suffix *-ous* represents the compound in the lower valence and *-ic* in the higher. The valence of iron in ferrous oxide, FeO, is 2 + and in ferric oxide, Fe_2O_3, 3 +. Both systems are in general use, and the name appropriate to the particular compound is learned in accord with conventional usage.

Reaction with Compounds. A number of compounds react with oxygen. Natural gas is composed chiefly of methane, a compound of carbon and hydrogen having the formula CH_4. The products of the combustion of methane are water and carbon dioxide.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$
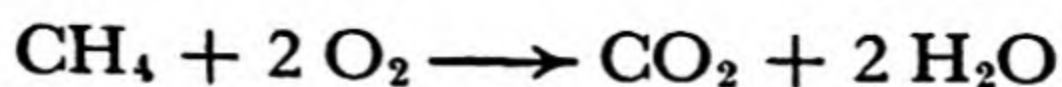
In general, a compound is found to react with oxygen if each of the component elements is combustible in the free state. Some elements react with oxygen in more than one ratio, forming different compounds. Thus, carbon yields two oxides. The oxide containing carbon in the lower valence reacts with an additional quantity of oxygen to form the oxide in which carbon has the higher valence.

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$
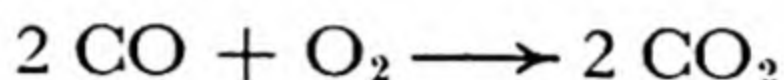
These two classes of substances do not include all of the compounds that react with oxygen, but they do include the most general types.

Energy Changes in Reactions of Oxygen. Most of the reactions of oxygen are accompanied by the evolution of heat. Substances that react vigorously with others are called *active substances*. At high temperatures, oxygen is relatively active toward many other substances. The most vigorous reactions evolve relatively large amounts of energy. Consequently, the products of such reactions contain smaller amounts of energy than the initial substances. The reaction of oxygen with carbon is highly exothermic, and the product, carbon dioxide, is relatively stable toward heat. The reaction of oxygen with mercury takes place slowly, and the heat of the reaction is small. Mercuric oxide is readily decomposed by heat. The reaction of oxygen with nitrogen is an endothermic reaction. Oxygen is not active toward nitrogen and the product, nitric oxide, contains a greater amount of energy than the uncombined gases. Consequently, nitric oxide is relatively unstable toward heat, and its decomposition is an exothermic reaction.

Combustion. An energetic reaction accompanied by a flame is called combustion. A flame is observed during the reaction of many gaseous substances with each other, but the name *combustion* is commonly understood to mean the burning of a substance in oxygen or air. Mixtures of combustible gases and oxygen explode when ignited if the proportions are within the required limits depending on the nature of the combustible gas. The reaction spreads through the whole of the material rapidly, and a large amount of heat is produced. The gaseous products expand and exert great force. Many disastrous explosions have occurred in coal mines and in buildings containing a gas and air mixture.

A combustible gas burns at a controlled rate when ignited as it is delivered from a suitable burner. Only one reaction occurs in a simple flame — as in the reaction of hydrogen with oxygen — and two zones may be observed. (Fig. 6.) The inner fuel zone contains the unburned gas, while the outer zone is the reaction area in which combustion occurs. Some gases, such as hydrogen and carbon monoxide, burn with an almost colorless flame, because the energy of the reaction is evolved for the most part in the form of heat.

Fig. 6. Simple Flame

The flame of a burning candle and of the common fuel gases is a complex flame. (Fig. 7.) At least three zones or cones may be observed. The inner fuel zone is similar to that in the simple flame. The next zone is an area of incomplete combustion. Hydrocarbons react in part to form water and finely divided particles of carbon. These particles become heated to incandescence, and this area of the flame is luminous.
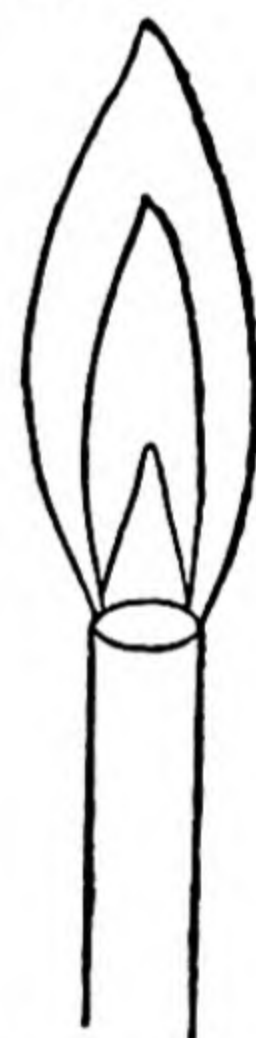
A deposit of free carbon in the form of soot collects if this cone of the flame is caused to impinge on a cold object. Outside the luminous area is the region of complete combustion. Enough air has become admixed to burn all of the combustible substances, and this region of the flame is nearly colorless. Luminosity of the flame is not always due to highly heated solid particles; direct emission of light occurs in some flames.

Fig. 7. Complex Flame

Gas Burners. The rate of reaction in a flame is increased by mixing air with the combustible gas before it reaches the end of the burner. This gives a smaller and hotter flame in which combustion is more nearly complete than in the complex flame of the burning candle. The Bunsen burner, assembled from the parts shown in Fig. 8, is the common type of burner for laboratory use. The gas is admitted

Fig. 8. Parts of Bunsen Burner

through the jet placed in the base of the burner. The barrel of the burner surrounds this jet, and air is admitted through the holes indicated. The proportion of air is regulated by the collar surrounding the lower end of the barrel. The mixture of air and combustible gas in the barrel of the burner must be delivered fast enough to keep the flame above the top of the burner. If the proportion of air in the gas mixture is correctly adjusted, a blue flame with well-defined cones may be observed. The hottest part of the flame, approximately 1800°, is near the tip of the middle cone. A luminous flame is produced with too small a proportion of air. Too large a proportion of air gives a leaner mixture, and the rate of combustion is so great that the flame strikes back, and the gas burns at the base of the burner. The burners on gas ranges and other household appliances operate on the same principle as the Bunsen burners used in laboratories.

Fig. 9. Méker Burner

When a wire gauze is held an inch or two above the top of a Bunsen burner, the gas may burn above the gauze without igniting the mixture below. The gauze conducts the heat away so rapidly that the gas underneath it does not get enough heat to become ignited. This principle is applied in the Fisher and Méker burners. (Fig. 9.) These burners are similar to the Bunsen burner, except that the barrel is much larger, the holes for the admission of air are larger, and a metal grid is placed over the top of the burner. More efficient gas-air mixtures, giving a hotter flame, may be used with such burners. The presence of the grid prevents the flame from striking back.
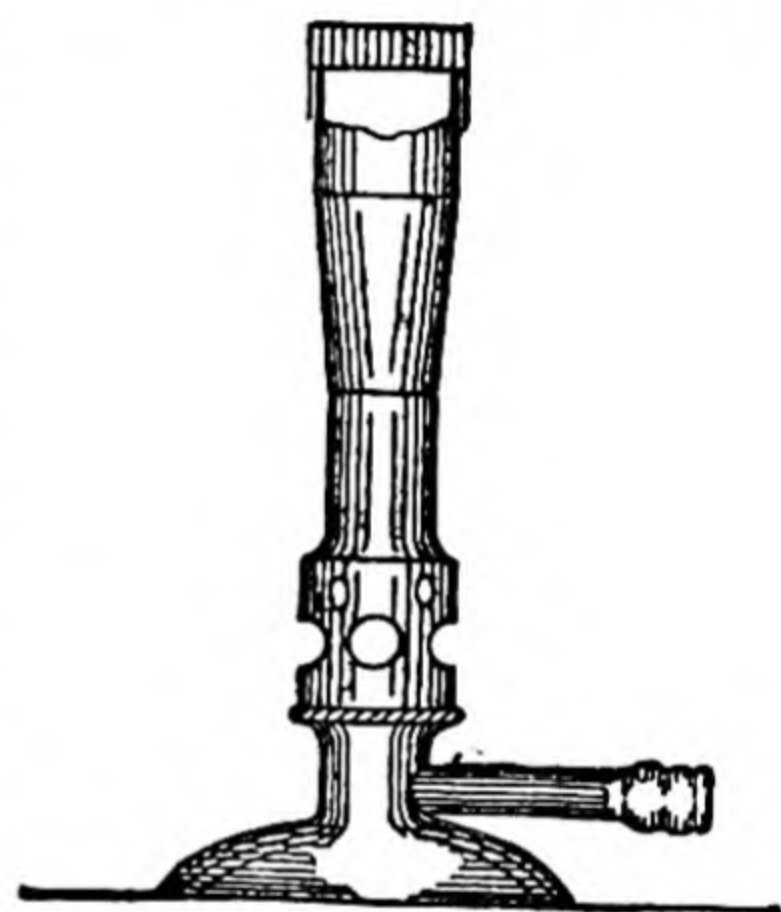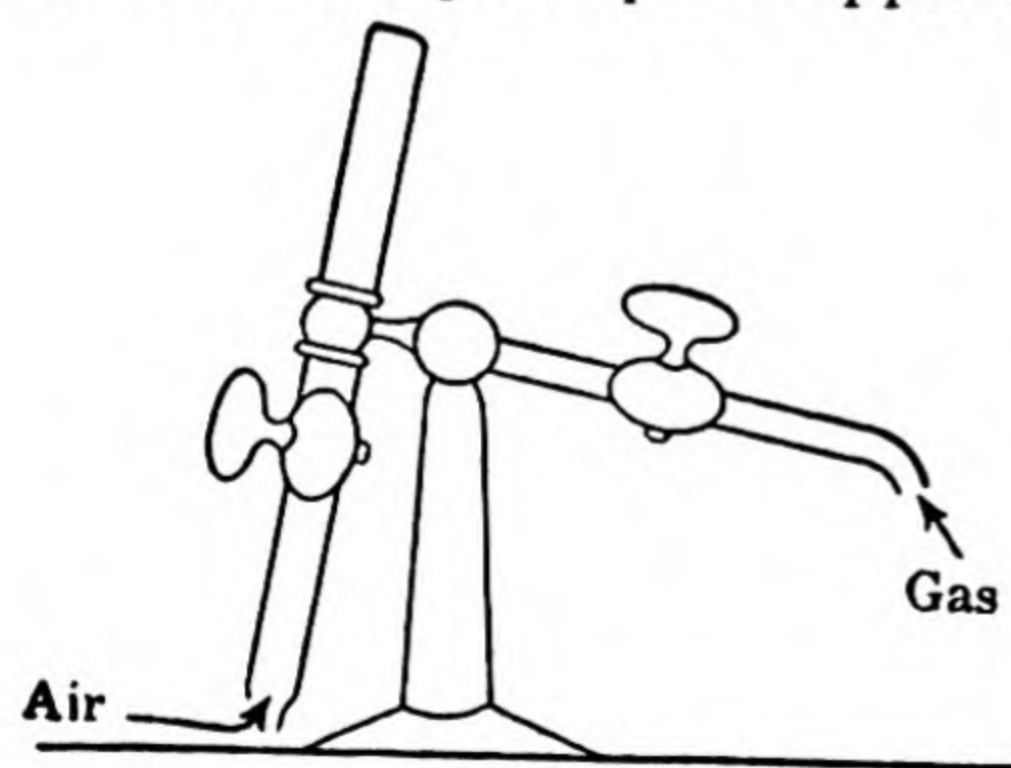
Fig. 10. Blast Lamp

In order to increase the rate of combustion in a burner still further, compressed air may be forced through an inner tube in

the burner and delivered along with the gas at the top of the burner. (Fig. 10.) This type of burner is called the blast lamp. A mixture containing a large proportion of air is burned very rapidly. The heat of combustion is liberated in a small area, and a hot flame is produced.

High-Temperature Flames. Air is commonly used to supply the oxygen required in combustion. For some purposes, a larger proportion of oxygen is desirable. The most extensive industrial use of oxygen is in the production of high temperatures in oxygen-gas flames, such as the oxyhydrogen and oxyacetylene flames.
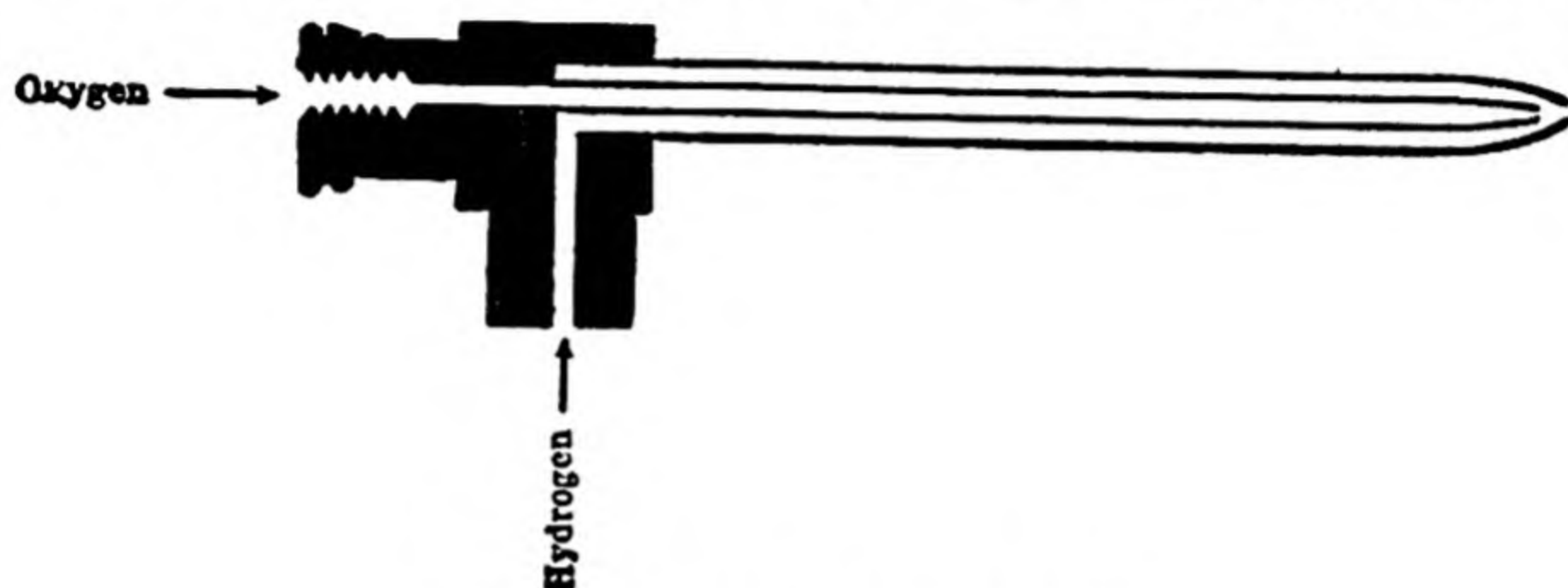
Oxygen →

Hydrogen ↑

Fig. 11. Oxyhydrogen Blowpipe

Oxygen instead of air is admitted through the inner tube of a burner similar to the blast lamp, in order to produce the hot flames used for the cutting and welding of metals. The oxyhydrogen blow-pipe (Fig. 11) was invented in 1801 by Robert Hare, a famous American scientist. The oxyhydrogen flame gives temperatures up to 2800°. The oxyacetylene flame is the most familiar and important of the high-temperature flames. The heat of combustion of acetylene, *i.e.*, the number of calories evolved per mole, is large.

$$2 C_2H_2 + 5 O_2 \longrightarrow 4 CO_2 + 2 H_2O + 624,000 \text{ cal.}$$
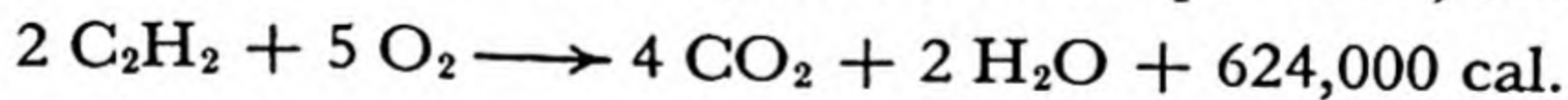
The reaction takes place rapidly in the oxyacetylene flame, and temperatures of 3500° may be obtained.

Respiration. During respiration, air is inhaled and oxygen is absorbed in the moist membrane lining the cells of the lungs. The dissolved oxygen passes through this membrane into the blood and combines with the haemoglobin in the red blood corpuscles. The circulation of the blood carries the oxyhaemoglobin to the various parts of the body, and the reactions of oxygen with differ-

ent substances supply heat to maintain body temperature and energy to accomplish work. Carbon dioxide, one of the products of these reactions, is transferred by the blood to the lungs and is exhaled. The per cent of carbon dioxide in the air contained in the lungs is normally about 5.5. This proportion of carbon dioxide aids in regulating the respiratory process. Patients suffering from respiratory diseases, such as pneumonia, may require larger proportions of oxygen than contained in air. Consequently, oxygen is supplied to meet this demand, and carbon dioxide is usually mixed in proper proportions with the oxygen for this purpose. Oxygen is administered along with the anaesthetic in anaesthetizing a patient for surgical operations. Oxygen is also used to maintain the requisite air composition for respiration in submarines and in airplanes at high altitudes.

Spontaneous Combustion. The same products result from the complete reaction of oxygen with a substance whether the reaction takes place slowly, as during rusting and decay, or rapidly, as during combustion. The same amount of energy is evolved for the same quantity of material. The difference in temperature is due to the difference in the rate at which heat is produced. Temperatures at which substances begin to burn vary with the nature of the substance. The kindling temperature for a specific material also varies depending on the size of the particles of a solid or liquid and the relative proportion of oxygen in the air. Many substances of low kindling temperature react fairly rapidly with oxygen of the air at ordinary temperatures. Such reactions are exothermic and cause a rise in the temperature, which in turn further increases the rate of reaction. If a substance of this type happens to be in a place where the air circulation is insufficient to convey the heat away, these effects may lead cumulatively to ignition. This is called spontaneous combustion. Cloths impregnated with certain oils, such as the linseed oil used in paint, may ignite spontaneously if they are left in a cupboard. Fine particles of coal may ignite spontaneously if left too long in storage bins. The ignition of some organic materials, such as damp hay, results from bacterial action, which generates heat and leads to the formation of spontaneously combustible products. The burning of these products causes in turn the combustion of the rest of the material.

Ozone. In 1785, Van Marum noticed a peculiar odor in the air near an electrical machine in operation. In 1840, Schönbein showed that this odor is due to a specific substance which he called ozone. Ozone is commonly prepared by subjecting oxygen to the silent discharge of electricity at high electrical potential. The apparatus may be constructed by using two concentric glass tubes with a coating of tinfoil on the outer side of the outer tube and the inner side of the inner tube. (Fig. 12.) These tinfoil layers are connected
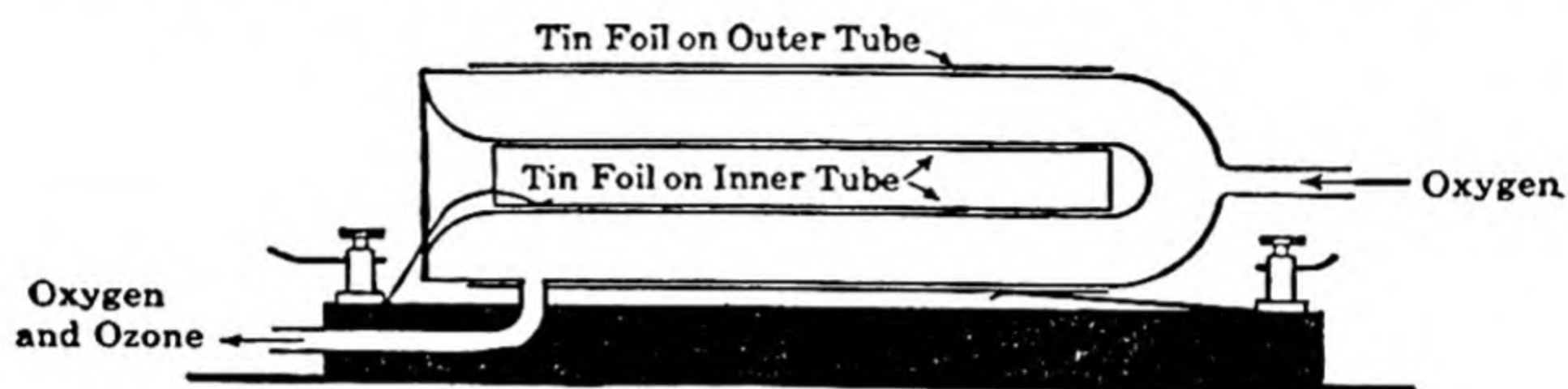
Fig. 12. Ozonizer

to the terminals of an induction coil, and oxygen is passed through the space between the tubes. When oxygen is cold and dry, the emerging gas mixture may contain as much as 7.5 per cent of ozone. Ozone is also formed from oxygen by the action of ultraviolet light.

Ozone has the characteristic pungent odor often noticed in the vicinity of electrical machines. The gas may be condensed to a blue liquid, which boils at $-112°$ and freezes at $-251°$. Ozone is composed of the same atoms as oxygen, but its density is 1.5 times the density of oxygen. The molecular weight of ozone is 48, showing that there are three oxygen atoms in the molecule. Thus, oxygen and ozone are different molecular modifications of the same element. *The different forms of an elementary substance in the same state are known as allotropes.* The formation of ozone from oxygen is a reversible endothermic reaction. *A reversible reaction is one in which the products interact to produce the initial substances.* This is shown in an equation by the use of two arrows pointed in opposite directions:

$$3\,O_2 + 69,000 \text{ cal.} \rightleftharpoons 2\,O_3$$
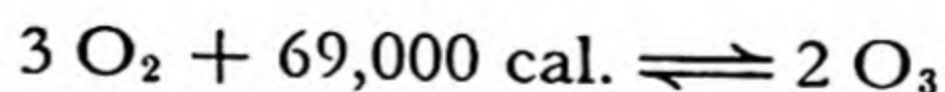
Ozone decomposes slowly at room temperature but rapidly at 250°. The reactions of ozone are of the same variety as those of oxygen, since the two allotropes contain the same kind of atoms, but the

ozone's activity is greater than the oxygen's. A greater amount of heat is produced in the reactions of ozone than in the corresponding reactions of oxygen.

$$3 C + 2 O_3 \longrightarrow 3 CO_2 + 352,170 \text{ cal.}$$
$$3 C + 3 O_2 \longrightarrow 3 CO_2 + 283,170 \text{ cal.}$$
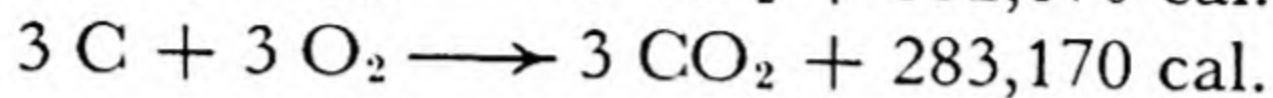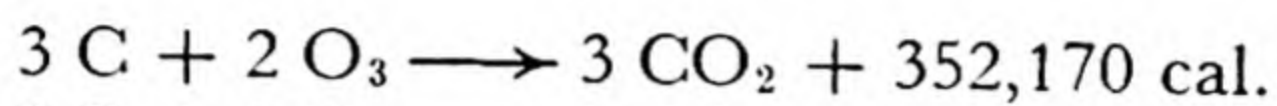
The difference in the two amounts of heat produced by the combustion of the same weight of carbon is equal to the heat absorbed in the conversion of three moles of oxygen into two moles of ozone.

Since ozone is more active than oxygen, it reacts with some substances not affected by oxygen at ordinary temperatures. Ozone reacts with metallic silver to form silver peroxide, Ag_2O_2, and oxygen.

$$2 Ag + 2 O_3 \longrightarrow Ag_2O_2 + 2 O_2$$
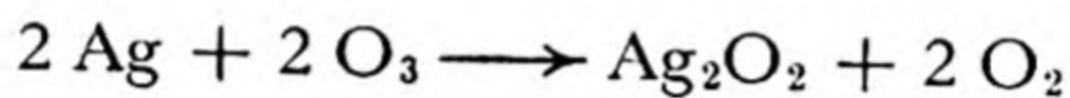
Ozone also reacts with a solution of potassium iodide, KI, containing starch to produce a blue coloration. The color is due to the interaction of starch with free iodine, formed by the reaction of ozone with potassium iodide. The other products of the reaction are potassium hydroxide and oxygen.

$$2 KI + H_2O + O_3 \longrightarrow 2 KOH + I_2 + O_2$$
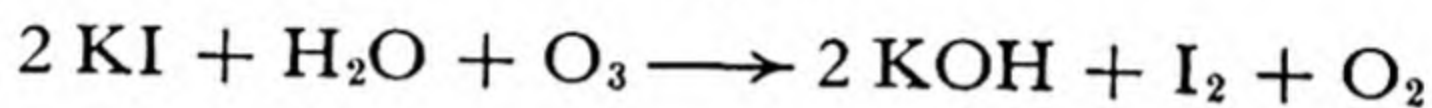
Oxygen is not active enough to produce free iodine by reaction with the potassium iodide solution.

Ozone has been used to a limited extent for disinfection of drinking water, because it destroys certain microorganisms. It is also used as a deodorant of air in crowded auditoriums, because it reacts with certain ill-smelling organic substances. Ozone finds further application in the bleaching of paper pulp, flour, and some fabrics.

Conditions Which Affect the Velocity of Reactions. The velocity of a reaction is altered by changes in conditions. Many substances do not react with oxygen noticeably at ordinary temperatures but burn vigorously when they are heated to high enough temperatures to start the reaction. The velocity of a reaction means the amount of the material undergoing change in unit time. The velocity of all reactions increases as the temperature is raised. This effect is not the same for all reactions, but, in many reactions the velocity is approximately doubled for each 10° rise in temperature.

Substances burn more rapidly in oxygen than in air. Air contains only about one fifth by volume of oxygen. Consequently, any specified volume contains nearly five times as much oxygen as an equal volume of air measured at the same temperature and pressure. *Concentration is the amount of a substance in unit volume.* The concentration of oxygen is nearly five times greater in pure oxygen than in air at the same temperature and pressure. The velocity of a reaction is increased by increasing the concentration of the reacting substances.

Finely divided solids react more rapidly than the same materials in a coarser state of aggregation. Wood shavings may be ignited more easily than large sticks of the same wood. The velocity of a reaction involving a solid or liquid is increased by dividing the substance into small particles so as to expose a larger surface area. Many finely divided combustible solids form explosive mixtures with air. Such substances react violently when a spark is introduced, and some of these mixtures become ignited spontaneously. Disastrous explosions have been caused by the ignition of dusts in wheat elevators, flour mills, and coal bins.

A fourth condition that affects the velocity of many reactions is the presence of a catalyst. Some catalysts accelerate reactions, while others retard them. Accelerating catalysts are used extensively in industrial processes to secure suitable reaction velocities at lower temperatures than would otherwise be required. The catalyst does not cause the reaction but affects its velocity. There are many reactions for which no catalysts have been discovered.

THE ATMOSPHERE

Some Greek philosophers considered air to be one of the fundamental elements. It is now generally known that air is a gaseous mixture composed primarily of oxygen and nitrogen, and that it contains also a number of additional components.

Components of the Atmosphere. Air contains nearly constant proportions of three elementary substances, *viz.*, nitrogen, 75.4 per cent; oxygen, 23.2 per cent; and argon, 1.2 per cent, by weight. It also contains small proportions of several other inactive gases and varying proportions of carbon dioxide, water vapor, and dust.

In particular localities, samples of air may contain still other gases as temporary components. The air in a closed garage where an automobile engine is running becomes contaminated by the highly poisonous gas, carbon monoxide. In the vicinity of sulfur water springs, the air contains a gas of disagreeable odor, hydrogen sulfide.

·A consideration of the composition and properties of air shows at once that it is a mixture. Although it is homogeneous and appears to contain nearly constant proportions of its principal components, the composition of air samples is not constant but varies at different times and places. Air may be liquefied, and the liquid shows the properties of a mixture. Its composition changes as the liquid boils, because the percentage of the components having lower boiling points is greater in the gas than in the liquid from which they escape. The elementary gases may be mixed in the same proportion as in air without energy change, which would accompany the formation of a compound.

Nitrogen in the Air. Nitrogen is a gas with very little chemical activity at ordinary temperature and pressure. It is the major component of the air, nearly four fifths by volume; and its presence in the air affects the rate at which oxygen reacts. Due to the action of bacteria in the soil, a large amount of nitrogen is converted into nitrogen compounds each year. Such compounds are essential to the growth of plants. During the decay of animal and vegetable matter containing nitrogen compounds, a portion of the nitrogen is returned to the air in the form of the free element. Under natural conditions and over a period of years, a balance is maintained between the consumption of nitrogen to form its compounds and the liberation of nitrogen by decay. The harvesting of agricultural crops containing nitrogenous substances removes them permanently from the soil where they grew and upsets this balance. Hence, fertilizers containing soluble nitrogen compounds must be applied to maintain the fertility of the soil. Within the past twenty years, the production of nitrogen compounds from atmospheric nitrogen has become the chief source of such substances, and this constitutes the principal use of atmospheric nitrogen. Nitrogen is obtained in nearly pure condition by separating it from the other gases in the air. This may be done by converting the air into a liquid, and

collecting separately the nitrogen gas which boils from this liquid mixture at a temperature below the boiling point of the oxygen.

The Oxygen and Carbon Dioxide Cycle. Carbon dioxide is produced by the respiration of animals, by the decay of animal and vegetable matter, and by the combustion of coal, fuel oils and gases, wood, and other fuels containing carbon. Consequently, the proportion of this gas in the air is greater in industrial areas than in rural sections. The average proportion is approximately 0.03 per cent, but in crowded rooms it may become as great as 1 per cent. Air containing proportions of carbon dioxide considerably greater than those normally present may be breathed safely, for it has no poisonous effects.

Despite these changes, which tend greatly to reduce the total quantity of oxygen in the air and to increase the quantity of carbon dioxide, the proportions of these two gases remain approximately constant, because natural processes having opposite effects tend to establish a balance. Plants absorb carbon dioxide from the air and convert it into cellulose and other related products by a reaction which releases oxygen to the air. Energy is absorbed in this reaction which takes place in sunlight under the influence of chlorophyll in the green leaves of the plant. The source of the energy is the sun, and the energy thus converted is stored for future use.

Water Vapor in Air. Liquid water evaporates when exposed to air. In a closed vessel, gaseous water accumulates in the air over the liquid, and some of it condenses to form the liquid again. These two changes are opposite in effect and, after a time, the two processes proceed at the same rate. *A closed system in which two processes of opposite effect proceed with the same velocity is in a state of equilibrium.* The concentration of water vapor in the air does not further change unless the temperature changes, and the space is saturated with water vapor. The per cent of water vapor required to saturate the air is much greater at high than at low temperatures. Consequently, when atmospheric conditions cause warm moisture-laden air to rise, it expands, and is cooled. But it no longer can retain in the gaseous state all the water it held at the higher temperature, and precipitation of the excess occurs in the form of rain, sleet, or snow. In this way, the soil's water content is replenished.

The relative proportion of water vapor in the air is usually stated in terms of *relative humidity, i.e.,* the ratio between the concentration of water vapor actually in the air and the concentration required for equilibrium at the same temperature. The average relative humidity found to be most comfortable is about 50–60 per cent. The relative humidity affects the rate of the evaporation of moisture from the skin. The normal temperature of a person in good health averages approximately 98.6° F. The reactions of various materials in the body with oxygen generate heat, which serves to maintain the body temperature. The excess is lost to a small extent by radiation and conduction, since the temperature of the surrounding air is usually below that of the body, but the regulation of body temperature is primarily due to evaporation of moisture. When the relative humidity is low, evaporation occurs rapidly. When the relative humidity is high, evaporation of water from the skin occurs slowly because the air is nearly saturated. The oppressiveness of a crowded room is due largely to excessive proportions of water vapor. When the air is not in circulation, the layer next to the body becomes nearly saturated. The ventilation of a room requires both a sufficient supply of fresh air and the circulation of the air. Air conditioning requires the regulation of both the temperature and the humidity at comfortable levels. This may involve the addition of relatively large quantities of water in winter, and the removal of large quantities of water on a humid summer day.

Dust in the Air. Dust in the air consists of solid particles of a number of substances so small that they do not readily settle. The presence of dust in the air is important in that dust particles serve as nuclei for the condensation of water vapor. In the absence of dust, the air would become supersaturated with water, and clouds and rain would be unlikely to form. Moisture would condense directly on the surfaces of solid objects, and umbrellas and roofs would be useless for keeping one dry.

Dust also includes minute living organisms, such as bacteria and spores of molds. When these settle upon dead organic matter, they lead to the process of decay by which nature disposes of such matter. Some of these microorganisms are not beneficent but lead to disease and infections.

The Inert Gases. In 1785, Cavendish noticed a small amount of a residual gas when oxygen and nitrogen had been removed from a sample of air. Lord Rayleigh, a British physicist, observed in 1895 that the residual nitrogen obtained from air by the removal of the other known atmospheric substances is more dense than nitrogen obtained by the decomposition of its compounds. Sir William Ramsay found that a residual gas — amounting to 0.933 per cent of the volume of the sample of air — resulted after the removal of all the gases known at that time. This material was found to enter into no chemical reactions and was named *argon.* Subsequently, it was found that this residual gas contains several other substances in very small proportions mixed with argon. These substances comprise a group of inert gases, known as the helium group: *helium, neon, argon, krypton, and xenon.* Radon, a product of the disintegration of radium, is also a member of this group, but it does not normally occur in air.

When liquid air is allowed to evaporate, different components predominate in the fractions obtained at different temperatures. It is possible to arrange the apparatus so as to secure several of the atmospheric gases in high enough concentration for industrial use. When an electric discharge passes through tubes containing neon at low pressure, a brilliant red light is emitted. Mercury vapor tubes give different color effects, and still different colors are secured by the use of gas mixtures and of tubes made of glass having special composition. The use of these tubes for electric signs has become familiar. Argon is used to fill electric light bulbs having tungsten filaments and thus prevent the rapid disintegration of the filament.

Helium. Examination of the spectrum of prominences of the sun, during an eclipse in 1868, led Lockyer to the discovery in the sun of a substance then unknown in terrestrial matter. To this substance the name *helium* was given. Hillebrand, in 1889, observed the liberation of a small quantity of an inactive gas during the reaction of certain uranium minerals with acids. He supposed that this gas was nitrogen. Ramsay repeated these experiments in 1895, while searching for sources of argon, and isolated an inert gas having low density. The spectrum of this gas was found to be the same as that observed by Lockyer. The amount of helium

obtained from uranium minerals is of no practical importance, nor is the proportion in the air sufficient for industrial extraction.

Next to hydrogen, helium has the lowest density. During World War I, Ramsay suggested the use of helium for the inflation of balloons and dirigibles. The buoyancy of helium is about 90 per cent of that of hydrogen, but helium has the advantage over hydrogen in being inactive. It was found that the natural gas in the Texas and Kansas gas fields contains a small percentage of helium, 1 or 2 per cent in some samples. Methods were developed for the separation of helium from this source, and production was started in Texas. The war ended before a sufficient supply for actual use had been secured. The production has been continued, and the methods of separation improved so that the cost has been greatly reduced. The dirigibles built for the United States Navy were inflated with helium. The only known commercial source of this element in useful quantities is under the control of the United States Government.

At the high pressures under which air must be supplied to divers, larger proportions of nitrogen are dissolved by the blood than usual. If the pressure is reduced too quickly when the diver comes to the surface, bubbles of the gas form in the blood stream. To prevent this condition, known as caisson disease or bends, the pressure must be decreased gradually in a pressure chamber, so that the dissolved nitrogen may be exhaled. The solubility of helium is much less than that of nitrogen, and, consequently, the length of time the diver must stay in the decompression chamber is greatly decreased if a mixture of oxygen and helium, in preference to air, is supplied to the diver while at work.

EXERCISES

1. How is oxygen prepared industrially? What factors determine the selection of an industrial method?
2. Describe the usual laboratory method for the preparation of oxygen. Why is this method selected in preference to others?
3. Calculate the weight of potassium chlorate required to produce 5 g. of oxygen; 5 liters of oxygen.
4. What is the importance of the fact that oxygen is slightly soluble in water?
5. Discuss the reactions of oxygen, and write equations for examples to illustrate each type.

6. What is meant by an exothermic reaction? an endothermic reaction? What is the relation between the energy changes in reactions and the stability of the products toward heat?
7. What is meant by combustion? kindling temperature? spontaneous combustion?
8. Discuss flames and gas burners. How are high temperature flames developed in the oxygen-gas blowpipes?
9. What are allotropes? Explain the similarities and differences in the reaction of oxygen and ozone.
10. Name four conditions which affect the velocity of reactions, and state the effect of each. Give examples to illustrate each of these effects.
11. Name the essential components of the atmosphere, and indicate the importance of each.
12. Give evidence to support the conclusion that air is a mixture.
13. What is meant by a state of equilibrium? a space saturated with water vapor? relative humidity?
14. What are the inert gases? Why are helium, neon, argon important?

SUPPLEMENTARY READINGS

Dampier-Whetham, W. C. D., *A History of Science*, The Macmillan Company, New York, 1930, pp. 195–99.

Moore, F. J., *History of Chemistry*, McGraw-Hill Book Company, Inc., New York, 1939, chaps. V–VI.

Smith, E. F., *Chemistry in America*, D. Appleton and Company, New York, 1914.

Ramsay, W., *Gases of the Atmosphere*, The Macmillan Company, New York, 1915.

Weeks, M. E., *The Discovery of the Elements*, Journal of Chemical Education, Easton, Pa., 1935, pp. 35–48; 278–91.

Jaffe, B., *Crucibles*, Simon and Schuster, Inc., New York, 1930, secs. III, IV, VI.

Read, J., *Prelude to Chemistry*, The Macmillan Company, New York, 1937.

Priestley Number, J. Chem. Education 4, 145–99 (1927).

"The Discovery of Oxygen," *Alembic Club Reprints, Nos.* 7–8, Oliver and Boyd, Edinburgh, 1923.

Carter, G. O., and H. F. Reinhard. "Modern Uses of Oxygen," *J. Chem. Education* **19**, 91 (1942).

"Oxygen," *Fortune* **XVI**, 2, 61 (1937).

Gross, F. P., Jr., "Rare Gases in Everyday Use," *J. Chem. Education* **18**, 533 (1941).

Chapter 4

TYPES OF COMMON SUBSTANCES
AND REACTIONS

The classification of substances into related groups is a great aid in learning and understanding the properties they exhibit. This chapter treats some of the general properties and reactions characteristic of several classes of substances together with the equations representing some types of common reactions. No attempt is made to discuss specific substances in detail. Some important members of each class are considered more fully in subsequent chapters.

The Elements. To the chemist, elements are simple substances, *i.e.*, an element is composed of atoms having the same chemical properties. Elements may exist in uncombined state and as constituents of compounds. The elements differ from each other in physical properties and in chemical behavior. They may be classified into two groups, *metals and nonmetals*. This classification is useful in describing the elements, because a number of general properties are associated with these names.

The physical properties of the metals depend on the structural arrangement of the atoms in the solid. The metals are commonly obtained in a crystalline form, in which the distances between the atoms are so small that the particles are in a *close-packed structure*. The metals in a compact condition possess luster, *i.e.*, they reflect light to a high degree. Sometimes metals appear to lack luster because of a tarnished surface layer, but the freshly cleaned and polished surfaces of the metals are lustrous. Another characteristic property of metals is their ability to conduct electricity without transfer of material from one part of the conductor to another. This property is so highly characteristic of the metals that it is called *metallic conductivity*. Metals differ greatly in their conductivity of electricity. Silver, copper, and gold are excellent conductors, but some metals, such as bismuth and antimony, are poor con-

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ductors. Some of the metals have high density, for example lead, mercury, gold, and tungsten, but sodium and potassium are less dense than water. There are also great differences in the mechanical properties of metals, malleability, ductility, and tensile strength.

In general, *the physical properties of the nonmetals* differ greatly from the properties of the metals. Although nonmetals may be obtained in crystalline forms, they are more commonly observed in a noncrystalline condition. Several of the nonmetals are gases at ordinary temperatures and pressures, and, as a class of elements, they have low melting points and boiling points. Furthermore, they commonly rank low in mechanical properties. The properties of the nonmetals cover a wide range, and the distinction between metals and nonmetals is not always sharply defined.

The number of metals and nonmetals is so large, and differences within each group are so great, that a further subdivision of the elements is desirable. The most useful classification of the elements is the *periodic system*. At this stage, the students' knowledge of the properties of elements is not sufficiently broad to afford a clear appreciation of this classification. Nevertheless, the periodic system may be employed as an empirical arrangement, and is discussed more fully in Chapters 12 and 13. The periodic system was first developed on the basis of a principle stated in 1869 by the Russian chemist, Mendeléef, as the **Periodic Law: The properties of the chemical elements are periodic functions of their atomic weights.** That is, when arranged in the order of their atomic weights, elements showing similar properties appear at regular intervals. A table may be arranged with similar elements grouped together in columns. Table 3 gives a greatly abbreviated form of this classification, in which some of the common elements are represented by their symbols. In a complete classification the blank spaces in the lines and columns are occupied by symbols of other elements. This list includes a sufficient number of elements to serve for the study of types of substances and their reactions. The numbers accompanying the symbols are the serial order numbers in which the elements appear in a complete list. The numbers heading each column show the group number and the common valences of the elements in their compounds.

TABLE 3. ABBREVIATED PERIODIC TABLE

I	II	III	IV	V	VI	VII
$1+$	$2+$	$3+$	$4-, 2+,$ $4+$	$3-, 3+,$ $5+$	$2-, 4+,$ $6+$	$1-, 1+,$ $3+, 5+,$ $7+$
H 1						
Li 3	Be 4	B 5	C 6	N 7	O 8	F 9
Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17
K 19	Ca 20		Ge 32	As 33		Br 35
Rb 37	Sr 38		Sn 50	Sb 51		I 53
Cs 55	Ba 56		Pb 82	Bi 83		

The elements represented by the symbols below and to the left of the diagonal line are metals, and those above and to the right are nonmetals. This list, with the elements in their respective groups and in the proper order within the group, should be committed to memory, because it is the basis of a systematic arrangement of much descriptive material.

Direct Union of the Elements. Many of the elements react with one another to form binary compounds. The reaction of oxygen with other elementary substances to produce oxides is discussed in the preceding chapter. Hydrogen unites with a number of the nonmetals to form hydrides. The valences of nonmetals in hydrides are the negative numbers shown in Table 3. Hydrogen reacts with the halogens, the elements in Group VII, to form hydrogen halides, for example, with chlorine to form hydrogen chloride.

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$
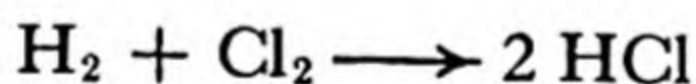
Hydrogen reacts with sulfur to form hydrogen sulfide and with nitrogen to form hydrogen nitride, commonly called ammonia.

$$H_2 + S \longrightarrow H_2S$$
$$3\,H_2 + N_2 \longrightarrow 2\,NH_3$$
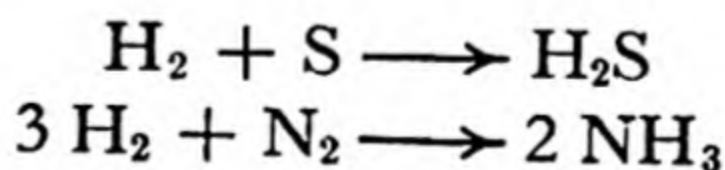
Most of the metals also react with the halogens and with sulfur. The following equations illustrate these reactions:

$$Ca + Br_2 \longrightarrow CaBr_2$$
$$2\,Al + 3\,Cl_2 \longrightarrow 2\,AlCl_3$$
$$Mg + S \longrightarrow MgS$$
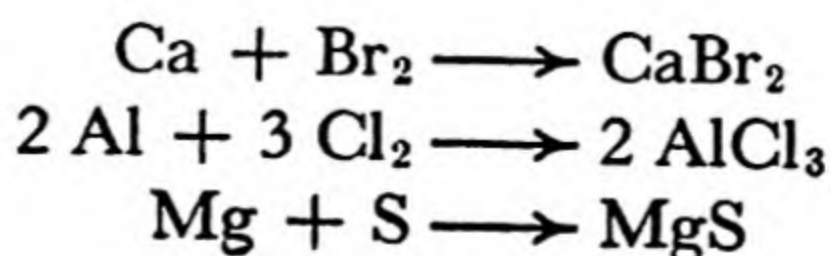
Many of the metals react with other nonmetals, such as nitrogen, phosphorus, and silicon.

$$3\,Ba + 2\,P \longrightarrow Ba_3P_2$$
$$3\,Mg + N_2 \longrightarrow Mg_3N_2$$
$$2\,Ca + Si \longrightarrow Ca_2Si$$
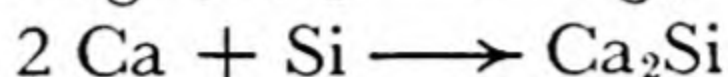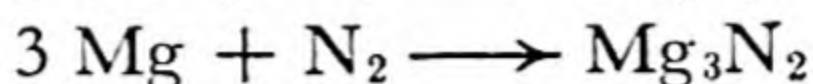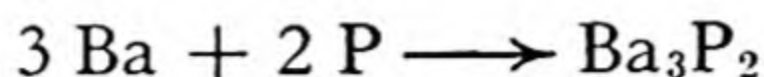
Some of the nonmetals react with other nonmetals forming binary products. In these compounds, the element from the higher numbered group in Table 3 has the negative valence, except in oxides. As a reference number in calculating valences, oxygen is assigned the number $2 -$ in all of its common compounds. Consequently, the other elements in these binary compounds have positive valences. Most of the nonmetals may exhibit more than one positive valence, depending on experimental conditions. Therefore, two or more compounds containing only the same two elements may be produced. Phosphorus reacts with chlorine to form the trichloride if an excess of phosphorus is present, and the pentachloride with an excess of chlorine.

$$2\,P + 3\,Cl_2 \longrightarrow 2\,PCl_3$$
$$2\,P + 5\,Cl_2 \longrightarrow 2\,PCl_5$$
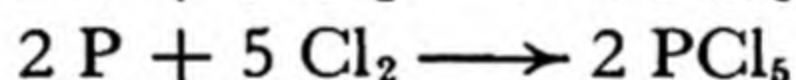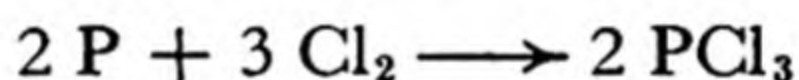
Sulfur reacts with oxygen to form both the dioxide and the trioxide.

$$S + O_2 \longrightarrow SO_2$$
$$2\,S + 3\,O_2 \longrightarrow 2\,SO_3$$
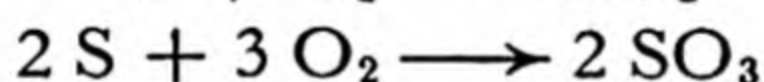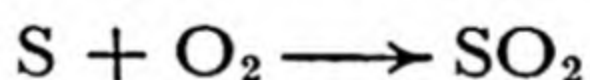
Reactions of Metal Oxides with Water. Several of the metal oxides react with water to form hydroxides. These reactions may also be regarded as combinations, for two substances interact to form a single product. A large amount of heat is produced in the reaction of the oxides of sodium, potassium, calcium, strontium, and barium with water. The products of these reactions are relatively stable toward heat unless very high temperatures are employed. The products of these reactions are called hydroxides because oxygen and hydrogen atoms make up radicals, which behave as unit particles in many reactions. The hydroxide radical has a valence of $1 -$. The type of reaction is illustrated by the following equations:

$$K_2O + H_2O \longrightarrow 2\,KOH$$
$$CaO + H_2O \longrightarrow Ca(OH)_2$$
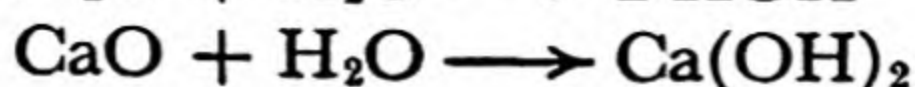
Some of the metal oxides, *e.g.*, silver oxide, react much less readily with water, and the reaction is incomplete, leaving much of the oxide unchanged. Most of the metal oxides do not react with water to an important degree. The metals forming oxides reacting vigorously with water are active, and their hydroxides are at least moderately soluble in water.

Properties of Solutions of Metal Hydroxides. Solutions of the metal hydroxides exhibit a number of properties in common. They produce characteristic colors with substances known as indicators. Thus, they cause red litmus to turn blue and colorless phenolphthalein to become red. The metal hydroxides react with acids and with the oxides of nonmetals to form water and a class of compounds known as salts. These reactions will be illustrated in subsequent paragraphs of this chapter. The metal hydroxides are called *basic hydroxides* because they comprise one of the groups of substances known as *bases*. The properties and reactions common to basic hydroxides are attributed to the hydroxide radical, which they supply as a reactive unit. The most extensively used soluble basic hydroxides are sodium hydroxide, potassium hydroxide, and calcium hydroxide.

Reactions of Nonmetal Oxides with Water. The oxides of many of the nonmetals combine with water to form acids. *Acids are compounds which contain replaceable hydrogen atoms.* Sulfur trioxide reacts with water forming sulfuric acid. This compound contains the sulfate radical with a valence of 2 −.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
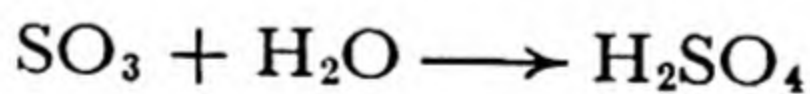
Similarly, phosphorus pentoxide reacts with water to form phosphoric acid.

$$P_2O_5 + 3 H_2O \longrightarrow 2 H_3PO_4$$
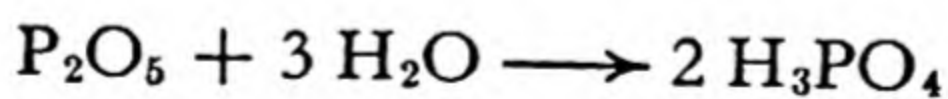
Nonmetal oxides that combine directly with water to form acids are called *acidic oxides*. They are also known as *acid anhydrides*. Some of the nonmetal oxides react only slowly and incompletely with water, while others show no appreciable reaction with water. Some of the nonmetals yield two acidic oxides and, consequently, two acids. When sulfur burns in air or oxygen, the main product is sulfur dioxide. The reaction of this oxide with water produces sulfurous acid. This acid is not stable at room temperature so that

the reverse reaction occurs along with the combination, and the reaction of sulfur dioxide with water is not complete.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$
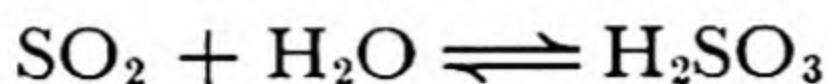
It is apparent from the examples noted above that a system is required for the naming of acids and other compounds derived from them. No change in the valence of the nonmetal is caused by reaction of the acidic oxide with water. The valence of sulfur is $4+$ in sulfur dioxide and also in sulfurous acid, and $6+$ in sulfur trioxide and sulfuric acid. The name of the common oxyacid — an acid, composed of hydrogen and a radical containing oxygen, in which the nonmetal has a high valence — is formed by adding the suffix -ic to a significant part of the nonmetal's name. The negative radical of the acid is the nonmetal-oxygen group combined with reactive hydrogen. In naming the radical, the suffix -ate replaces -ic in the name of the acid. The acid, H_2SO_4, is sulfuric acid, and the radical (SO_4) is the sulfate radical. The formula, HNO_3, represents nitric acid and (NO_3), the nitrate radical. The oxyacid of the nonmetal in its next lower common valence is named by the use of the suffix -ous and the corresponding radical by the suffix -ite. The formula, H_2SO_3, represents sulfurous acid and (SO_3), the sulfite radical; HNO_2 represents nitrous acid and (NO_2), the nitrite radical. In some acids the molecule contains a larger proportion of oxygen than in the common oxyacid. The prefix *per-* is used in naming such acids. An acid in which the molecule contains a smaller proportion of oxygen than the -ous acid is named by using the prefix *hypo-*. Acids which contain only the two elements, hydrogen and the nonmetal, are named by the use of the prefix *hydro-* and the suffix -ic. The significance of this system of names is illustrated by the acids containing chlorine.

Hydrochloric acid	HCl
Hypochlorous acid	$HClO$
Chlorous acid	$HClO_2$
Chloric acid	$HClO_3$
Perchloric acid	$HClO_4$

The association of the name and formula of the acidic oxide with the acid to which it corresponds is very important. A few of these relationships are shown in Table 4. The student should commit

this list to memory and should write equations for all of the reactions suggested by the list.

TABLE 4. COMMON ACIDIC OXIDES AND CORRESPONDING ACIDS

Sulfur dioxide	SO_2	Sulfurous acid	H_2SO_3
Sulfur trioxide	SO_3	Sulfuric acid	H_2SO_4
Carbon dioxide	CO_2	Carbonic acid	H_2CO_3
Phosphorus trioxide	P_2O_3	Phosphorous acid	H_3PO_3
Phosphorus pentoxide	P_2O_5	Phosphoric acid	H_3PO_4
Arsenic trioxide	As_2O_3	Arsenious acid	H_3AsO_3
Arsenic pentoxide	As_2O_5	Arsenic acid	H_3AsO_4

Additional examples are shown in Table IV in the Appendix.

Properties of Solutions of Acids. Solutions of acids cause blue litmus to turn red and produce no color effect with colorless phenolphthalein. They characteristically have a sour taste. Acids also react with many of the metals producing salts and in many instances free hydrogen. *A salt is a compound resulting from the replacement of the hydrogen of an acid by a metal or a metallic radical.* Some of the acids, *e.g.*, nitric and hypochlorous acids, do not commonly yield free hydrogen in their reactions with metals. Acids also react with the oxides and the hydroxides of the metals, forming water and corresponding salts. The characteristic properties and reactions of acids are due to the replaceable hydrogen atoms they contain. There are a number of other hydrogen compounds that do not have the properties of acids. Some of the acids are commonly prepared by reactions of acidic oxides with water, but other reactions are also employed in the preparation of acids. The acids commonly used as laboratory reagents are sulfuric acid, H_2SO_4, nitric acid, HNO_3, hydrochloric acid, HCl, and acetic acid, $HC_2H_3O_2$. Only one of the four hydrogen atoms in the molecule of acetic acid is replaceable. Hence, the formula is written as shown.

Displacement Reactions. The reaction of a metal with an acid, producing free hydrogen and a salt of the metal, is a reaction of displacement. During such reactions, atoms of the free element displace an equivalent number of atoms of some other element in the compounds. Zinc reacts with dilute sulfuric acid to form hydrogen and zinc sulfate and with hydrochloric acid to form hydrogen and zinc chloride.

$$Zn + H_2SO_4 \longrightarrow H_2 + ZnSO_4$$
$$Zn + 2\,HCl \longrightarrow H_2 + ZnCl_2$$
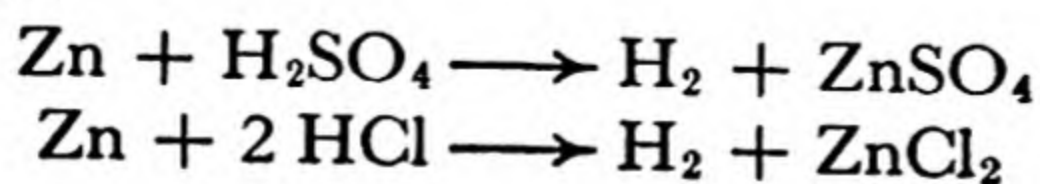
Hydrogen is not produced by the reaction of metals with hot concentrated sulfuric acid, but sulfur dioxide is the gaseous product. Magnesium and aluminum react with dilute sulfuric acid, producing hydrogen and the sulfates of these metals.

$$Mg + H_2SO_4 \longrightarrow H_2 + MgSO_4$$
$$2\,Al + 3\,H_2SO_4 \longrightarrow 3\,H_2 + Al_2(SO_4)_3$$
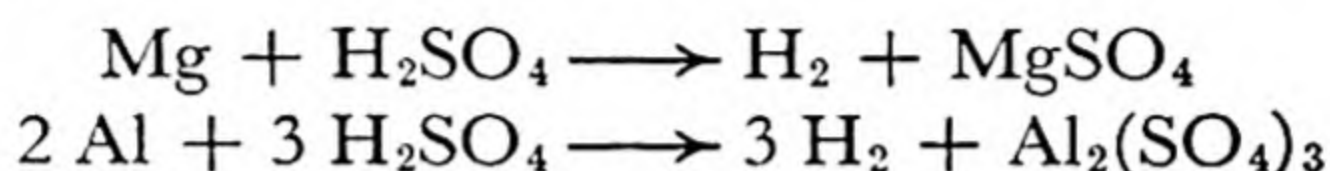
The salts formed by these reactions are soluble in water, but they may be obtained in the solid state by evaporating water to the concentration at which crystallization of the salt occurs.

A number of metals do not displace hydrogen from acidic solutions. The activity of such metals is not great enough. The metals may be subdivided on the basis of their activities into two groups, *viz.*, those displacing and those not displacing hydrogen from acids. The relative activity of the metals within each of these groups may also be determined experimentally, and they may then be arranged in a series showing decreasing activity. In the accompanying list some of the metals are arranged on this basis. A more inclusive list appears in Table V in the Appendix. Metals above hydrogen in this list displace hydrogen from acids such as dilute sulfuric acid and hydrochloric acid. Those which are below hydrogen do not displace it. Under the proper experimental conditions, each metal displaces those which follow it in the list. Some of the metals are so active that they cannot be displaced from aqueous solutions of their compounds, but instead, hydrogen may be displaced from water. Zinc displaces copper from solutions of cupric sulfate, and copper displaces silver from solutions of silver nitrate.

Activity of the Metals

Potassium
Calcium
Sodium
Magnesium
Aluminum
Zinc
Iron
Tin
Lead
Hydrogen
Antimony
Bismuth
Copper
Mercury
Silver
Gold

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$$
$$Cu + 2\,AgNO_3 \longrightarrow 2\,Ag + Cu(NO_3)_2$$
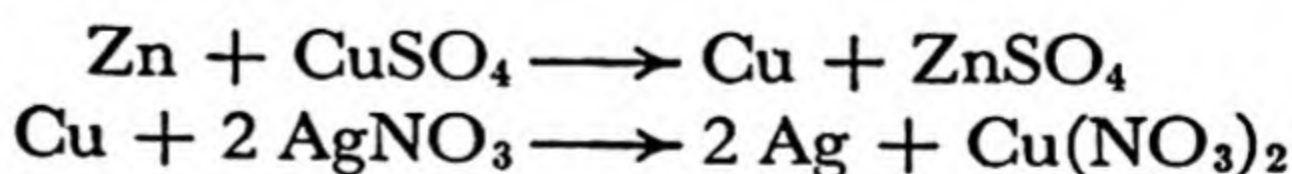
In similar reactions, some of the more active nonmetals displace other nonmetals of lower activity from solutions of suitable compounds. Chlorine displaces bromine from bromides and sulfur from sulfides.

$$Cl_2 + 2\,KBr \longrightarrow Br_2 + 2\,KCl$$
$$Cl_2 + Na_2S \longrightarrow S + 2\,NaCl$$
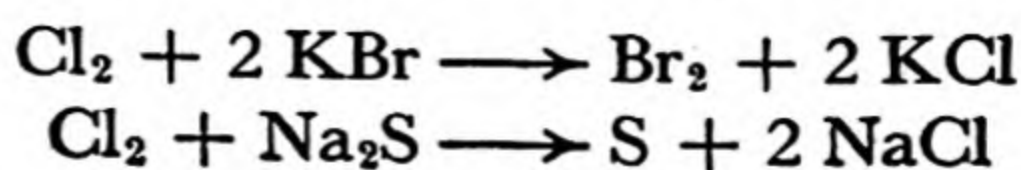
Double Decomposition Reactions. A reaction in which two compound substances interact in such a manner that two different products are formed is called a *double decomposition*. *An exchange of corresponding parts of the two substances occurs during such reactions.* The reaction of acids with metal hydroxides is a general reaction of this type. The properties characteristic of both the acids and the basic hydroxides disappear when equivalent quantities of the two substances react. A solution containing no excess of either the acid or the basic hydroxide is known as a *neutral solution*. The reaction of the acid with the basic substance in such proportions that a neutral solution is produced is *neutralization*. When hydrochloric acid is added to a solution of sodium hydroxide containing phenolphthalein as an indicator, the red color becomes faint as most of the hydroxide reacts. If acid is now added drop by drop with constant stirring, a condition is reached where the last trace of color is destroyed by the addition of a single drop. The solution is now virtually neutral. The evaporation of this solution leaves a white crystalline residue of sodium chloride, common salt. The reaction is represented by the equation:

$$HCl + NaOH \longrightarrow H_2O + NaCl$$
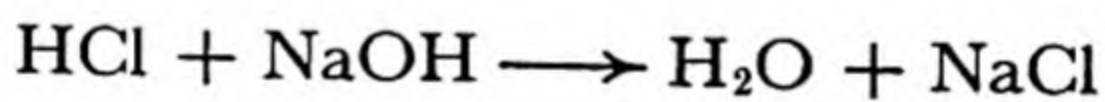
Other acids and basic hydroxides react with each other in a similar manner to form water and corresponding salts. The combination of the active hydrogen of the acid with the hydroxide radical of the basic hydroxide is common to all of these reactions, and this is the essential change that occurs during neutralization. Consequently, the quantity of the acid and the basic hydroxide entering into the reaction is such as to furnish hydrogen and the hydroxide radical in the ratio required for the formation of water. The following equations represent additional examples of this important type of reaction.

$$HNO_3 + NaOH \longrightarrow H_2O + NaNO_3$$
$$H_2SO_4 + 2\,KOH \longrightarrow 2\,H_2O + K_2SO_4$$
$$2\,H_3PO_4 + 3\,Ba(OH)_2 \longrightarrow 6\,H_2O + Ba_3(PO_4)_2$$
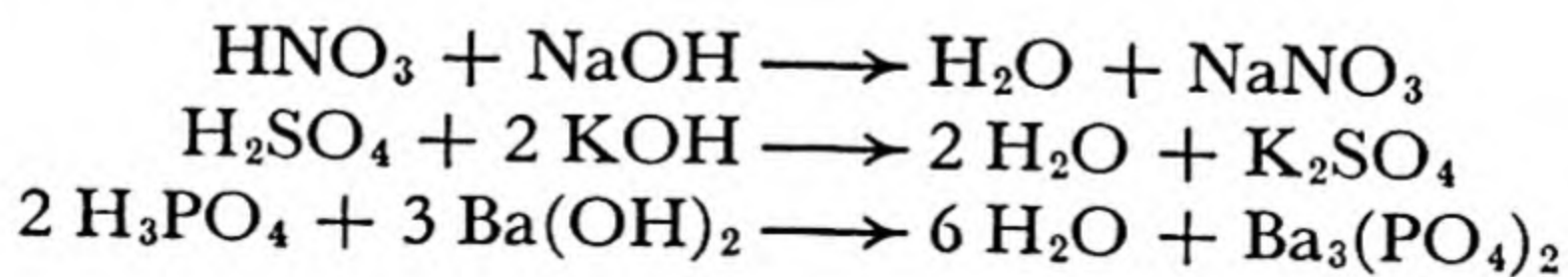
There are a number of double decomposition reactions involving other classes of substances. When solutions of silver nitrate and sodium chloride are mixed, a white, curdy, insoluble solid separates.

The solid is silver chloride, containing silver from the silver nitrate and chlorine from the sodium chloride. A solid product separating from a solution during a chemical reaction is called a precipitate. The other product of this reaction is sodium nitrate, which is soluble and is not observed in the course of the reaction. The formation of a precipitate is frequently indicated in equations by the use of a small downpointing arrow beside the formula of the substance.

$$AgNO_3 + NaCl \longrightarrow AgCl \downarrow + NaNO_3$$
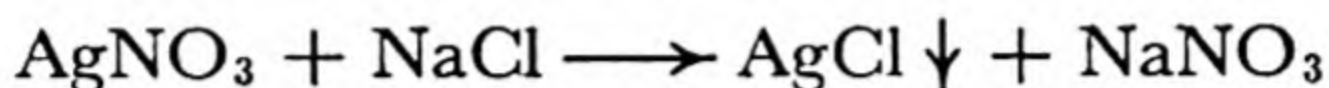
The formation of a precipitate causes double decomposition between the substances in the solution. Lead iodide is precipitated by the reaction of lead nitrate with potassium iodide in solution and silver chromate by the reaction of silver nitrate with potassium chromate.

$$Pb(NO_3)_2 + 2 KI \longrightarrow PbI_2 \downarrow + 2 KNO_3$$
$$2 AgNO_3 + K_2CrO_4 \longrightarrow Ag_2CrO_4 \downarrow + 2 KNO_3$$
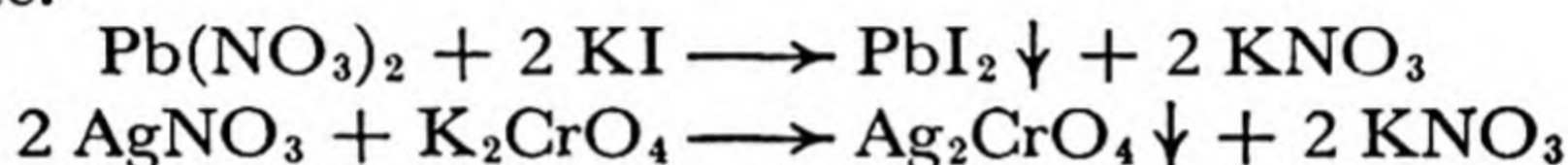
Reactions of Acids with Metal Oxides. The reactions of acids with oxides of metals are closely related to the reactions of acids with hydroxides of metals. In these reactions also water and salts of corresponding acids are formed. Hydrochloric acid reacts with cupric oxide to form water and cupric chloride.

$$2 HCl + CuO \longrightarrow H_2O + CuCl_2$$
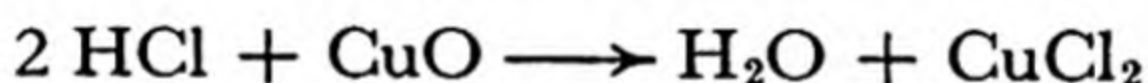
Sulfuric acid yields water and the sulfates when it reacts with magnesium oxide and with aluminum oxide.

$$H_2SO_4 + MgO \longrightarrow H_2O + MgSO_4$$
$$3 H_2SO_4 + Al_2O_3 \longrightarrow 3 H_2O + Al_2(SO_4)_3$$
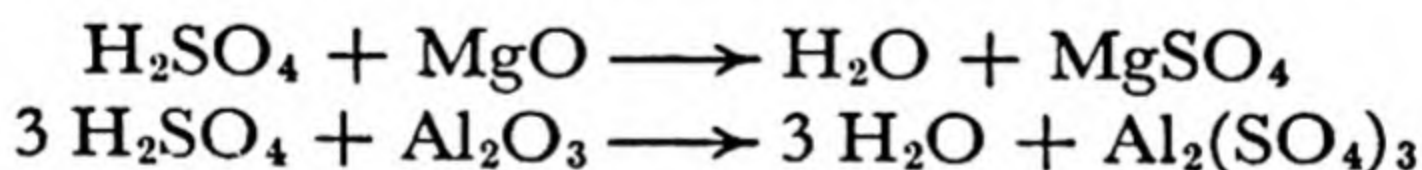
The proportion of acid and metal oxide in this type of reaction is such as to furnish two atoms of hydrogen for each atom of oxygen, the ratio in water. Oxides that react with acids, combining with the active hydrogen to form water, are called *basic oxides*. A few of these oxides also react with water to form basic hydroxides, as noted in a preceding paragraph. The elements which yield basic oxides are *metals*.

Reactions of Nonmetal Oxides with Basic Hydroxides. The reactions of nonmetal oxides with basic hydroxides are closely related to the two types of reactions of acidic substances with basic substances already considered. Some of these substances react at

ordinary temperatures, while others must be heated together to cause reaction. The products are water and the salt containing the oxyradical corresponding to the acidic oxide. Carbon dioxide reacts with sodium hydroxide to form water and sodium carbonate in the proportions shown in the equation:

$$CO_2 + 2\,NaOH \longrightarrow H_2O + Na_2CO_3$$
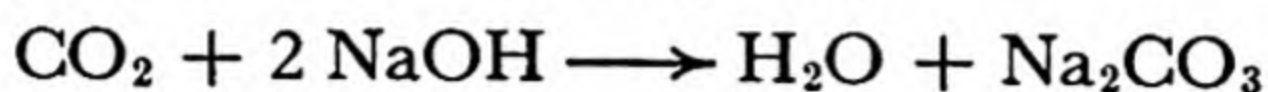
Phosphorus pentoxide reacts in a similar manner to form water and a phosphate, a salt of phosphoric acid.

$$P_2O_5 + 3\,Ca(OH)_2 \longrightarrow 3\,H_2O + Ca_3(PO_4)_2$$
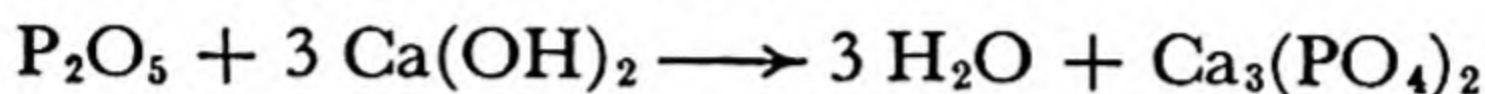
These reactions are typical of many nonmetal oxides with the more active basic hydroxides. The acidic oxides are oxides of nonmetallic elements.

Reactions of Nonmetal Oxides with Basic Oxides. The combination of acidic oxides with basic oxides to produce salts is a consequence of the acidic nature of the nonmetal oxides and the basic nature of metal oxides. When carbon dioxide gas is passed in contact with solid calcium oxide at ordinary temperatures, calcium carbonate is formed.

$$CO_2 + CaO \longrightarrow CaCO_3$$
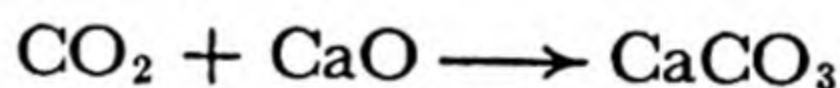
The reaction of silicon dioxide and calcium oxide requires that the substances be heated together. The product is calcium silicate.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$
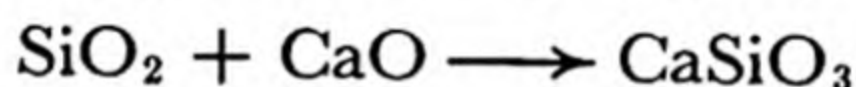
EXERCISES

1. Contrast in parallel columns the typical properties of metals with those of nonmetals.
2. State the law applied in the classification of elements in related groups, and explain the meaning of this law.
3. What is meant by a reaction of direct union? Write equations to represent the reaction of each of the following elements with oxygen and with chlorine: (a) zinc; (b) iron; (c) magnesium; (d) copper; (e) arsenic; (f) mercury; (g) phosphorus.
4. List several common properties of basic solutions, of acidic solutions.
5. A white powder may be either the oxide of calcium or the oxide of phosphorus. How could you determine by experiment which it is? Write equations for the reactions you apply.
6. Write equations to represent the reaction of each of the following oxides with water: (a) calcium oxide; (b) phosphorus trioxide; (c) sulfur trioxide; (d) barium oxide; (e) arsenic pentoxide.

7. What is meant by a displacement reaction? Write equations to represent the reaction of each metal in the following list with each of the acids.

Magnesium	Hydrochloric acid
Aluminum	Cupric sulfate
Zinc	Phosphoric acid
Iron	Silver nitrate

8. What are double decomposition reactions? What is meant by precipitation? Referring to a table of solubilities for the selection of suitable materials, write equations to represent five reactions producing precipitates.

9. Write equations to represent the reaction of each of the basic hydroxides in the following list with each of the acids.

Sodium hydroxide	Sulfuric acid
Calcium hydroxide	Phosphoric acid
Aluminum hydroxide	Nitric acid
Barium hydroxide	Acetic acid

10. Write equations to represent the reaction of each of the metal oxides in the following list with each of the acidic substances.

Magnesium oxide	Sulfur trioxide
Aluminum oxide	Nitric acid
Calcium oxide	Phosphorus pentoxide
Cupric oxide	Sulfuric acid

11. Write equations to represent the reaction of each of the acidic oxides in the following list with each of the basic substances.

Carbon dioxide	Barium oxide
Sulfur trioxide	Sodium hydroxide
Phosphorus pentoxide	Calcium hydroxide
Silicon dioxide	Potassium hydroxide

Chapter 5

STATES OF MATTER. THE KINETIC THEORY

The state of matter in which a substance exists under ordinary natural conditions of temperature and pressure is a characteristic property. A substance is commonly observed in more than one state if the temperature and pressure at which the change in state occurs lie within the range of general experience. Thus, the substance water is well-known in each of the three states. *The transition point* at which a change in state occurs is described in terms of the temperature and the pressure at which the two forms may remain together in equilibrium, *i.e.*, the condition at which the rate of change from one state to another is equal to the rate of the opposite change. *A transition temperature* is, therefore, the temperature at which equilibrium is maintained under specified pressure, usually the standard atmospheric pressure. The transition points for changes in state are characteristic physical properties of substances.

Most of the common substances may be converted from one state to another by changing the temperature and pressure. Some substances require substantial changes in conditions to bring about a change in state. Oxygen, hydrogen, and nitrogen were long considered to be permanent gases because no one had been able to liquefy them. Hydrogen was first liquefied by Dewar in 1898. The boiling point of the liquid is $-252.8°$. Helium was liquefied by Onnes in 1908, and its boiling point is $-268.9°$. Naturally, the liquefaction of these gases could not be caused until methods of securing very low temperatures were developed. Tungsten has a melting point of 3370° so that its familiar form is the solid. Some substances decompose when they are heated in the effort to cause a change in state. Such substances are known in only one or two of the three states of matter. Thus, potassium chlorate melts at 368° but decomposes at about 400°, and therefore a gaseous form of this substance is not known.

The physical properties of a substance differ greatly in the different states. Different substances in the same state exhibit a number of similar properties. Such properties have to do with the state of matter rather than any specific substance. There are, however, specific differences that depend on the nature of the substance. The properties of substances in the gaseous state show a greater degree of uniformity than liquids and solids. Hence, the gaseous state is discussed before the other states. The properties of gases serve as the basis of the kinetic theory, which is useful in accounting for the behavior of substances in all three states and for the phenomena which accompany the transitions from one state to another.

765
760
755

THE GASEOUS STATE

A quantity of gas has no definite shape or volume, but expands to fill completely and uniformly any closed vessel in which it is placed. Gases may be mixed in any proportion to produce a homogeneous mixture, unless they react with each other. The gases in a mixture do not separate, even though the densities of the single substances under similar conditions may differ greatly. Matter in the gaseous state is characterized by relatively low density, high compressibility, great expansibility, and low viscosity, *i.e.*, low resistance by one portion of a gas to flow over or through another portion. Two gaseous substances placed in the same container diffuse rapidly to form a mixture of uniform composition.

Gas Pressures. A gas exerts pressure on the wall of the vessel in which it is enclosed. The force per unit of area is the pressure. The pressure of a gas at fixed temperature depends on its concentration, that is, the quantity in unit volume. The pressure of the atmosphere may be measured by a barometer. (Fig. 13.) A simple barometer may be set up by filling a glass tube, approximately a meter in length and sealed at one end, with mercury. The tube is now inverted with the unsealed end beneath the surface of mercury in an open jar, taking care that

Fig. 13.
Barometer

no air is admitted. It is observed that mercury drops away from the closed upper end of the tube leaving a vacuum. The height of the mercury column above the level of the liquid in the jar is a measure of the atmospheric pressure. The average pressure of the atmosphere at sea level at 45° latitude is equivalent to a column of mercury approximately 760 mm. in height. This pressure is selected as a unit of pressure and is called *one atmosphere*. It is equal to 1033 g. per square centimeter. The actual atmospheric pressure may vary at different times and places, but the pressure of one atmosphere is an arbitrary, definite standard of pressure.

The Gas Laws. The volumes of gas samples vary in a uniform manner with changes in temperature and pressure. In the measurement of quantities of matter in the gaseous state, four factors are significant, *viz.*, weight or quantity, volume, temperature, and pressure. The gas laws state the relationships between these factors in a quantitative manner. The gas laws do not hold strictly for any known substance under all conditions of temperature and pressure, but they are sufficiently accurate for practical purposes when the changes cover a small range. In order to determine the effect of each of these variable factors, two may be held constant while the relations between the other two are measured. If the temperature and pressure of the gas do not change, the volume of a specific gaseous substance varies directly with the quantity. Since equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules, the molecular concentration does not change and the volume is a direct measure of the quantity in moles at constant temperature and pressure.

The Relation of the Volume to the Pressure of a Gas. Boyle's Law. In order to determine the effect of changes in pressure on volume, a definite quantity of gas is used and measurements are made at constant temperature. With these restrictions, it is found that

760 mm.

Fig. 14

doubling the pressure of a gas reduces the volume to one half (Fig. 14), and that reducing the pressure to one half doubles the
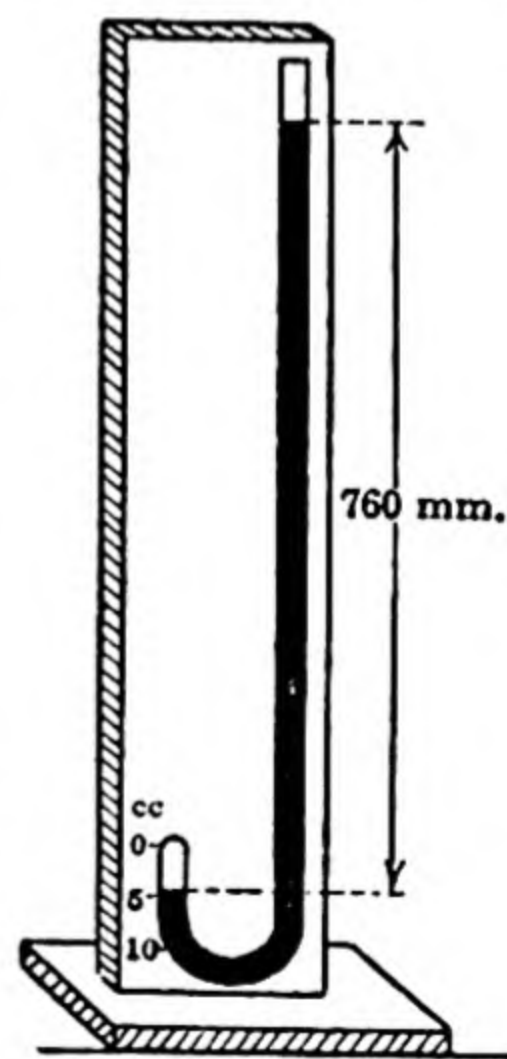
volume. Robert Boyle published the results of his measurements dealing with this relationship in 1662. The results are summarized in the generalization known as **Boyle's Law: At constant temperature, the volume of a given quantity of a gas varies inversely with the pressure.** This law is stated mathematically by the expression

$$V \propto \frac{1}{P}$$

By the introduction of the proportionality factor K, the formula becomes:

$$PV = K$$

The relationship between the volume and the pressure is shown graphically by the curve in Fig. 15, where V represents the volume in liters and P the pressure in atmospheres.

Boyle's law may be applied in calculating the effect of changes in pressure on the volume of a gas sample at constant temperature. The product of the volume and the pressure is constant. Therefore, the volume under changed pressure is calculated by multiplying the measured volume by a fraction showing the ratio of the pressures. If the new pressure is higher, the new volume must be smaller than the original, and the smaller pressure value is the numerator of the fraction. Conversely, if the new pressure is lower, the greater pressure is the numerator. If a gas sample occupies a volume of 152 ml. (milliliter) at a pressure of 740 mm., the volume it would occupy at 760 mm. and constant temperature is:
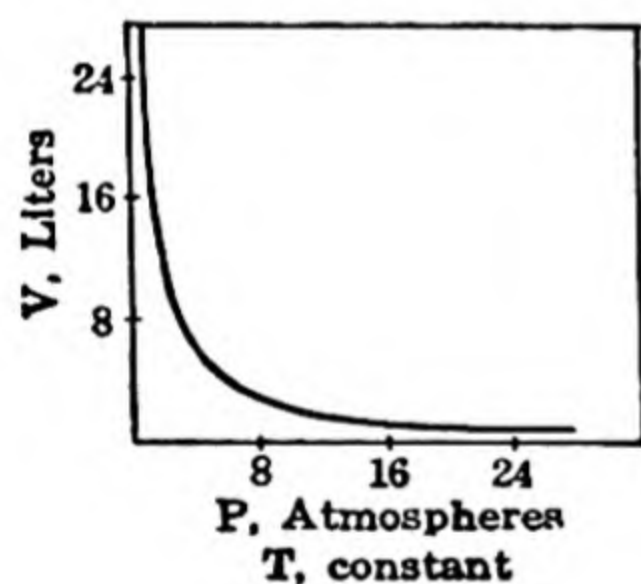
P, Atmospheres
T, constant

Fig. 15

$$V = 152 \times \tfrac{740}{760} = 152 \times 0.973 = 148 \text{ ml.}$$

If the original pressure had been 770 mm., the new volume at 760 mm. would be:

$$V = 152 \times \tfrac{770}{760} = 152 \times 1.013 = 154 \text{ ml.}$$

The Relation of the Volume to the Temperature of a Gas. Charles' Law. It is a familiar observation that hot air rises. This is due to the fact that air expands with rise in temperature and becomes less dense. Careful measurements show that the change in

volume of a fixed quantity of gas at constant pressure is equal to
1/273 of its volume at 0° for each degree change in temperature.
Should this uniform change in volume continue during the cooling
of a gas to very low temperatures, the gas sample would have no
volume at − 273°, because the contraction in volume would now
be 273/273 of its volume at 0°. This re-
lationship is shown graphically for four
gases in Fig. 16. The broken lines repre-
sent the extension of the curves based on
experimental data. These curves appear
to intersect at − 273°. This point rep-
resents the *absolute zero of temperature*,
− 273.18°, at which a gas theoretically
would have no volume. Since all gases
liquefy at temperatures above − 273°
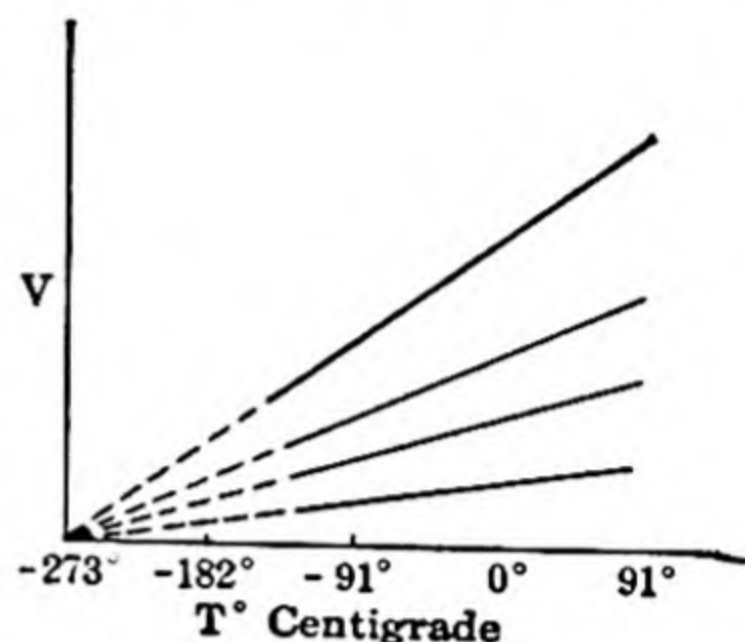
Fig. 16

(in round numbers), no physical significance is attached to the
zero volume of gas. Temperatures on the centigrade scale are
converted to the absolute scale by adding 273. Absolute tempera-
tures are commonly designated by the letter A or by K from the
name of Lord Kelvin. The temperature 20° C. is 293° A. The
effect of temperature changes on gas volumes was measured inde-
pendently by Charles and by Gay-Lussac, in 1801. The generaliza-
tion describing this effect is known as **Charles' Law** and also as
**Gay-Lussac's Law: At constant pressure, the volume of a given
quantity of a gas varies directly with
the absolute temperature.** Mathemati-
cally, this relation is:

$$V \propto T \quad \text{or} \quad V = KT$$

The relation between the temperature
and the volume of a gas sample is shown
graphically in Fig. 17.

Fig. 17

The volume which a measured gas
sample would occupy at some different
temperature may be calculated by the application of this law.
The volumes at the two temperatures are in the same ratio as
the absolute temperatures. Therefore, the observed volume is
multiplied by the fraction that shows the ratio of temperatures.
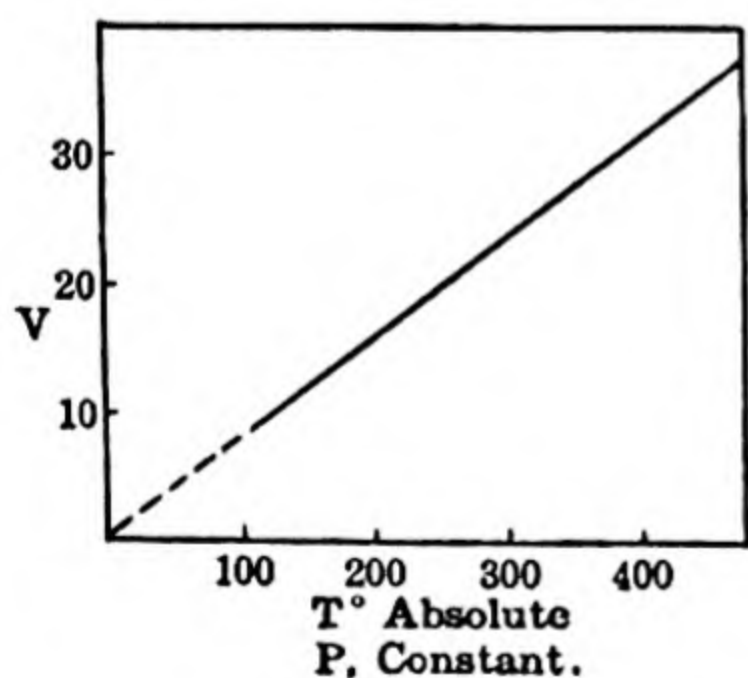
If the new temperature is higher, the new volume will be greater than the original, and the larger of the absolute temperatures is the numerator of the correction fraction. Conversely, if the new temperature is lower, the larger temperature value is the denominator. If a gas sample occupies a volume of 100 ml. at a temperature of 20°, the volume it would occupy at 0° and constant pressure is:

$$V = 100 \times \tfrac{273}{293} = 100 \times 0.932 = 93.2 \text{ ml.}$$

The Relation of the Temperature to the Pressure of a Gas. The effect of changes in temperature upon the pressure of a gas sample is derived from the laws of Charles and Boyle. Suppose that a gas sample is confined in a cylinder with a movable piston and that a constant pressure of one atmosphere is applied to the piston. (Fig. 18.) If the temperature is raised from 0° to 273°, the piston
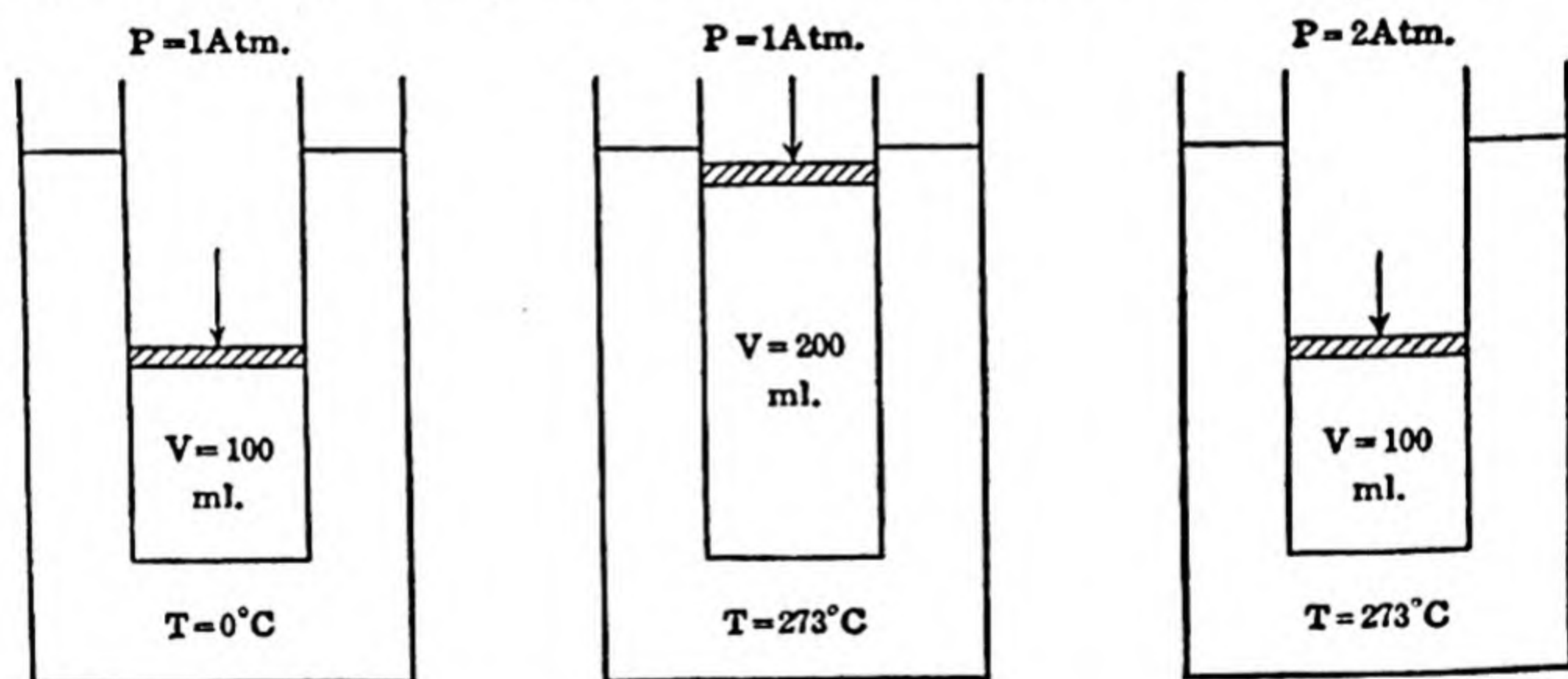
Fig. 18

moves to permit the expansion of the gas to double its former volume, and it is necessary to double the pressure applied to the piston in order to compress the gas to its former volume. **At constant volume, the pressure exerted by a fixed quantity of a gas varies directly with the absolute temperature.** If the gas sample were collected at 20° and 760 mm., the pressure in the same volume at 100° would be:

$$P = 760 \times \tfrac{373}{293} = 760 \times 1.273 = 967 \text{ mm.}$$

The General Gas Equation. A general equation relating the weight and the volume of a gas to temperature and pressure may be derived from the specific gas laws just considered. The volume

of a quantity of gas varies directly with absolute temperature and inversely with pressure.

$$V \propto \frac{T}{P}$$

Introducing a proportionality factor,

$$V = K \frac{T}{P}$$

or
$$PV = KT$$

If this equation is applied specifically to one mole of a gas, the molar gas constant R may be substituted for the proportionality factor K.

$$PV = RT$$

The factor n representing the number of moles is now introduced in order to make the equation more general.

$$PV = nRT$$

The numerical value of the gas constant is calculated from experimental data. One mole of any gas occupies 22.414 liters at 0°, 273.1° A., and a pressure of one atmosphere. These numbers are now substituted in the equation which may be solved for the evaluation of R.

$$R = \frac{PV}{nT} = \frac{1 \text{ atmosphere}}{1 \text{ mole}} \times \frac{22.414 \text{ liters}}{273.1°}$$
$$= 0.08207 \text{ liter-atmosphere per mole per degree}$$

This equation is useful for the solution of problems dealing with weights and volumes of gaseous substances. It is necessary to remember that the weight is expressed in moles, the pressure in atmospheres, the temperature on the absolute scale, and the volume in liters. The volume occupied by 10 g. of oxygen at 20° and 740 mm. may be calculated according to this equation. The weight of oxygen is $\frac{10}{32}$, 0.3125 mole; the pressure $\frac{740}{760}$, 0.973 atmosphere; and the absolute temperature is 293°.

$$V = \frac{nRT}{P} = \frac{0.3125 \times 0.08207 \times 293}{0.973} = 7.721 \text{ liters}$$

Partial Pressures of Gases in a Mixture. The gas laws describe the relations of pressure, volume, and temperature for gas mixtures also. In 1801, Dalton investigated the pressure of mixed gases. The results of his experiments are summarized in the **Law of Partial Pressures. The pressure exerted by a gas mixture is equal to the sum of the pressures of the components of the mixture.** The pressure of each gas in a mixture is equal to the pressure it would exert if it were present alone in the containing vessel. The partial pressure of each gas in a mixture is proportional to its relative concentration. If a mixture of oxygen and nitrogen contains these gases in a molar concentration ratio of one to four, the partial pressure of oxygen in this mixture is one fifth, and of nitrogen four fifths, of the total pressure. Slightly soluble gases are usually

p gas - pAtm.   pgas < pAtm.   pgas > pAtm.
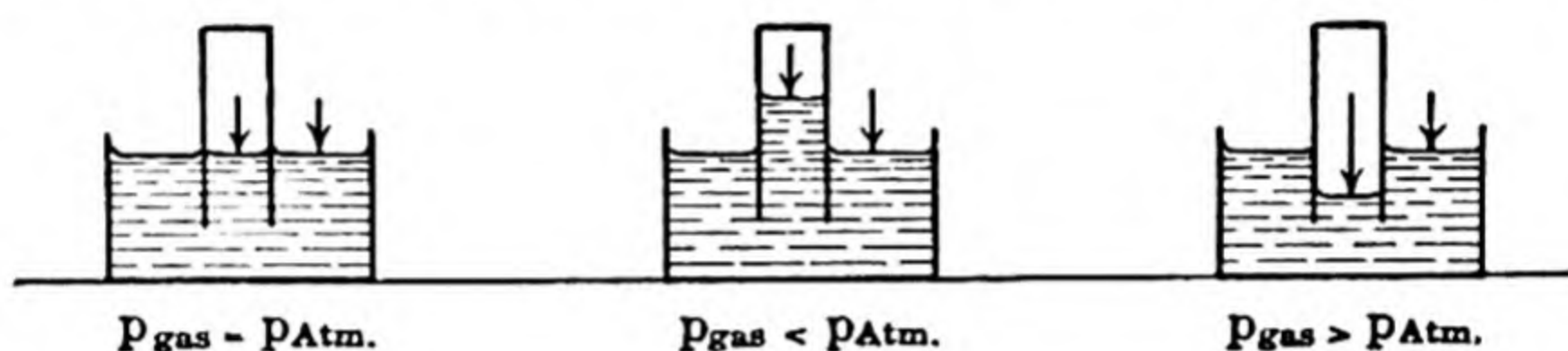
Fig. 19

collected over water, as illustrated by the collection of oxygen in Fig. 5. When the liquid is at the same level both inside and outside of the collecting jar, the pressure of the enclosed gas is equal to the atmospheric pressure. This is shown diagrammatically in Fig. 19. The gas collected in this manner is saturated with water vapor. The pressure of saturated water vapor is constant at each temperature and increases with rise in temperature. The pressures of saturated water vapor are shown in Table II in the Appendix.
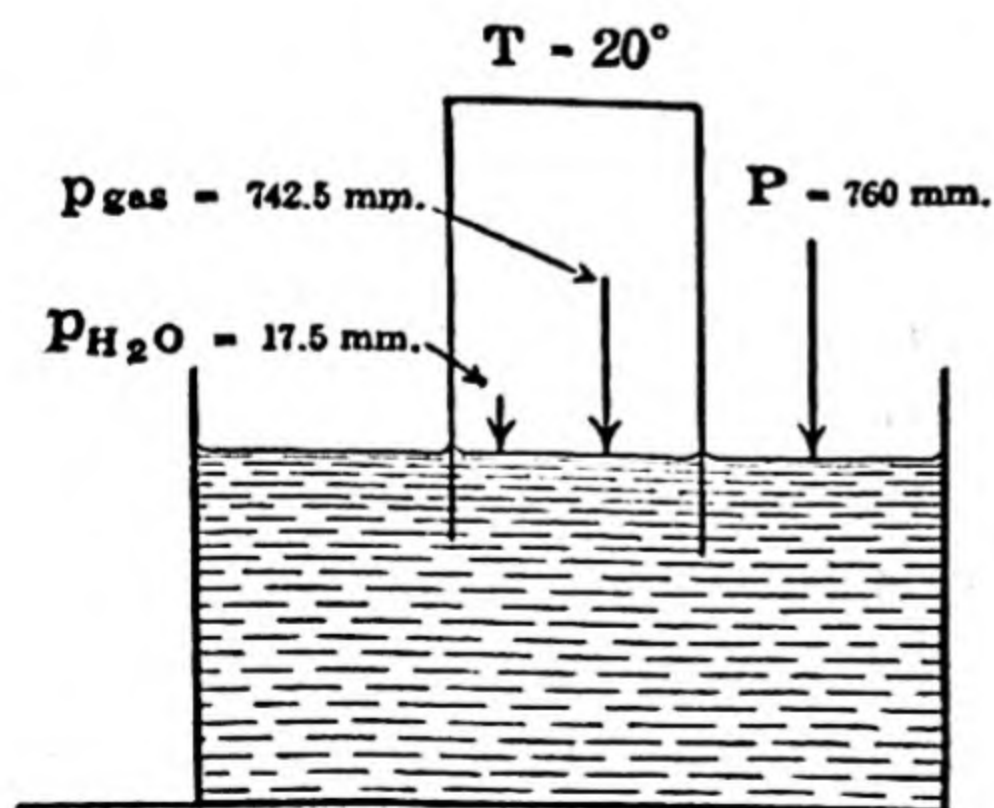
$T - 20°$

$p_{gas} - 742.5$ mm.

$p_{H_2O} - 17.5$ mm.

$P - 760$ mm.

Fig. 20

Suppose that a sample of oxygen is collected over water at 20° and a barometric pressure of 760 mm. The sum of the partial pressure of oxygen, p_{O_2}, and the partial pressure of water vapor, p_{H_2O}, is equal to the total pressure, 760 mm. (Fig. 20.)

$$p_{O_2} + p_{H_2O} = P = 760 \text{ mm.}$$
$$p_{O_2} = 760 - 17.5 = 742.5 \text{ mm.}$$

If dry oxygen were present in this volume, the pressure would be 742.5 mm., not 760 mm.

Correction of Gas Volumes for Changes in Temperature and Pressure. Since the volume occupied by a definite quantity of a substance in the gaseous state varies greatly with changes in temperature and pressure, it is customary to express the volume under specified conditions. These conditions, called *standard conditions*, are a pressure of 760 mm. and a temperature of 0° C., 273° A. The actual measurement of the volume of the gas is more conveniently made at some other temperature and pressure. The volume is then corrected to standard conditions by the application of the two correction factors described separately under pressure and temperature effects. Suppose that the volume of a sample of pure gas is 150 ml. at 20° and 752 mm. The volume of this gas under standard conditions would be:

$$V = 150 \times \tfrac{752}{760} \times \tfrac{273}{293} = 150 \times 0.989 \times 0.932 = 138.3 \text{ ml.}$$

If, however, the gas is collected over water, the pressure due to water vapor must be taken into account, and the corrected pressure must be used in the calculation of the new gas volume.

$$\text{Corrected pressure} = 752 - 17.5 = 734.5 \text{ mm.}$$
$$V = 150 \times \tfrac{734.5}{760} \times \tfrac{273}{293} = 150 \times 0.966 \times 0.932 = 135 \text{ mm.}$$

The volume of a gas saturated with water vapor at a specified temperature and pressure may be calculated in the same manner. The volume of a given quantity of dry oxygen is 200 ml. under standard conditions of temperature and pressure. The volume it would occupy if collected over water at 20° and 757.5 mm. is calculated in the following manner:

$$p_{O_2} = 757.5 - 17.5 = 740 \text{ mm.}$$
$$V = 200 \times \tfrac{760}{740} \times \tfrac{293}{273} = 200 \times 1.027 \times 1.073 = 220.4 \text{ ml.}$$

The Diffusion of Gases. If two gases which do not react with each other are introduced into the same container, they diffuse rapidly to form a uniform mixture throughout the entire vessel. In 1832, Graham measured the relative rates of diffusion of a num-

ber of gases. **The rates of diffusion of gases at the same temperature vary inversely with the square roots of their densities.** *Density is defined as mass per unit volume*, but the weight of one milliliter of gas is so small that the weight of one liter is often used to express the density. The densities of oxygen and hydrogen are in the ratio of sixteen to one; and the rates of diffusion of these gases are in the ratio of one to four.

The Kinetic Theory of Gases. The uniform behavior of gases under changing conditions of temperature and pressure indicates that all gases have similar structure. The theory of the constitution of gases, which accounts for their behavior on a mechanical basis, was first proposed by Bernouilli in 1738. It has been supplemented by additional experimental data and has been verified beyond reasonable doubt. The fundamental assumptions of this theory, known as the kinetic theory, may be stated in the following postulates:

> *Gases are composed of separate particles, molecules. Relative to their sizes, the molecules are very far apart.*
>
> *The molecules of gases are in rapid motion, colliding with each other and with the walls of the containing vessel.*
>
> *The molecules of gases are perfectly elastic, and no loss of energy results from molecular collisions.*
>
> *The molecules of gases exert no appreciable attraction for one another at ordinary pressures.*
>
> *The motion of the molecules is a manifestation of heat energy. The average kinetic energy of all of the molecules of a gas is proportional to the absolute temperature.*

The great compressibility of gases indicates a porous structure in which the molecules themselves occupy an inappreciable fraction of the total volume of the gas. The compression of a gas involves crowding the molecules somewhat more closely together. The pressure exerted by a gas is due to the impacts of the molecules on the walls of the container. The fact that the pressure of a gas does not diminish on standing indicates that the molecules rebound from each collision with other molecules and with the walls of the vessel, retaining undiminished kinetic energy.

The average distance through which a molecule moves between

collisions is called the *mean free path.* This distance averages about one thousand times the diameter of the molecules, when the pressure is equal approximately to normal atmospheric pressure. Gases may diffuse rapidly into one another because of the rapidity with which the molecules are moving, the large amount of free space, and the lack of attraction of the molecules for each other. The great expansibility of gases is explained by the fact that the molecules are in rapid motion and that the kinetic energy of the molecules is so great that the forces of attraction are relatively insignificant.

Kinetic Interpretation of the Gas Laws. The compression of a gas crowds the molecules into a smaller volume. When the volume of a gas is reduced to one half, the molecular concentration is doubled. (Fig. 21.) The average number of molecular impacts upon the unit area of the wall of a containing vessel in unit time is now doubled. The average force of each impact is not altered, and consequently, as stated in Boyle's law, the pressure is doubled.

The average kinetic energy of gas molecules is constant at fixed temperature. Hence, the pressure of a gas mixture depends on the total number of molecules in unit volume, not the nature

Fig. 21

of the molecules. The partial pressure exerted by each gas in the mixture depends on the per cent of its molecules, *i.e.,* upon the relative value of the molecular concentration of the gas.

Changes in temperature alter the kinetic energy of the molecules by changing the velocity with which they move. A rise in temperature increases the rate of molecular motion, with the result that both the frequency and the force of the impact of the molecules on the walls of the container are increased. The absolute zero of temperature would represent the cessation of molecular motion, and the average kinetic energy of the molecules is proportional to the absolute temperature. Therefore, the pressure of a gas sample at constant volume varies directly with the absolute temperature.

The light molecules of a gas of low density have the same kinetic energy at a specific temperature as the heavier molecules of a gas
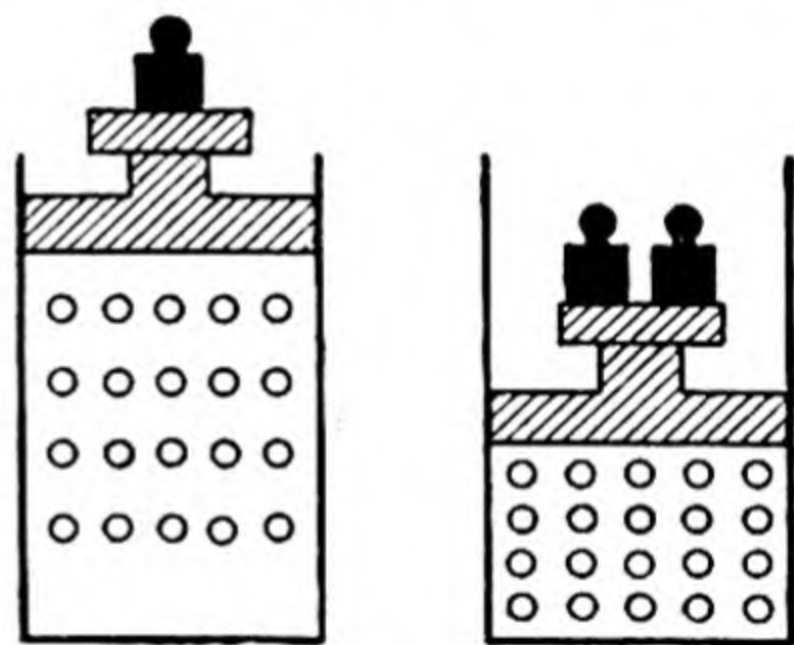
of greater density. Consequently, the lighter molecules travel with the greater velocity. It is found from a study of kinetic energy relationships that the velocities of the molecules of two different gases at the same temperature vary inversely with the square roots of their densities. The relative rates of diffusion of two gases depend on the comparative velocity of their molecules. The velocity of the hydrogen molecule at 0° is 1.84 kilometers, approximately 1.15 miles, per second, and the velocity of the oxygen molecule is about 0.46 kilometer per second. For comparison, the velocity of sound is 0.331 kilometer per second at 0°, and the earth's orbital velocity is approximately 29.8 kilometers per second.

At a fixed temperature, the total kinetic energy of all of the molecules in a gas sample is constant, since the product PV is constant. In equal volumes of two gases at the same temperature and pressure, the total kinetic energy of the molecules in one gas is equal to that in the other. The total kinetic energy of the molecules in a gas sample is equal to the product of the average kinetic energy of the molecules and the number of molecules. The average kinetic energy of the molecules of all gases is the same at the same temperature. Consequently, the number of molecules in equal volumes of different gases at the same temperature and pressure is the same. Thus, it follows that Avogadro's hypothesis is confirmed by a consideration of the kinetic energies of gas molecules.

Deviations from the Gas Laws. Most gases exhibit deviations from the behavior described by the gas laws, even at ordinary temperatures and pressures. The greater the changes, the greater are the deviations from the gas laws. A gas whose behavior is in strict accord with the general gas law equation would be a *perfect* or *ideal gas*. In such a gas, the product of the pressure and volume would be constant at fixed temperature as shown by the horizontal line in Fig. 22. For most gases this product decreases at first with increasing pressure and then increases, as indicated by the curves for oxygen and carbon dioxide. This indicates two causes leading to deviation from Boyle's law, one, usually more significant at the lower pressures, and the other, at the higher pressures. The two effects counterbalance each other at some intermediate pressure, as shown by the intersection of the curves for oxygen and carbon dioxide with the curve for the ideal gas. The curve for hydrogen

shows no decrease in the product of pressure and volume at 0° but an increase throughout the entire range.

At low pressures, gases are dilute forms of matter, the molecules are far apart, and the forces of molecular attraction are insignificant. The forces of attraction become greater as the molecules are brought closer together, thus causing a greater contraction than predicted by Boyle's law. This effect is greater for gases composed of molecules with stronger forces of attraction for each other, and less for gases in which these forces are very slight.

A second deviation is due to the volumes of the molecules themselves. As the concentration of the gas molecules increases in consequence of increasing external pressures, the molecular volume becomes a larger fraction of the total volume of the gas. Under high pressures, the amount of free space in the gas is much less than under low pressures, and the effect of further increases in pressure is less than calculated.

Fig. 22. Deviations from Boyle's Law

These deviations are not great enough to prohibit the application of the gas laws for small changes in temperature and pressure. Furthermore, correction factors may be introduced into the general gas law equation to account for these effects if they are large enough to be significant.

THE LIQUID STATE

The liquid state is intermediate between the solid and gaseous states, and the properties of liquids show similarities to those of both solids and gases. Liquids undergo transitions into the other states.

A fixed quantity of a liquid has definite volume at a specific temperature and does not expand to fill uniformly all containing
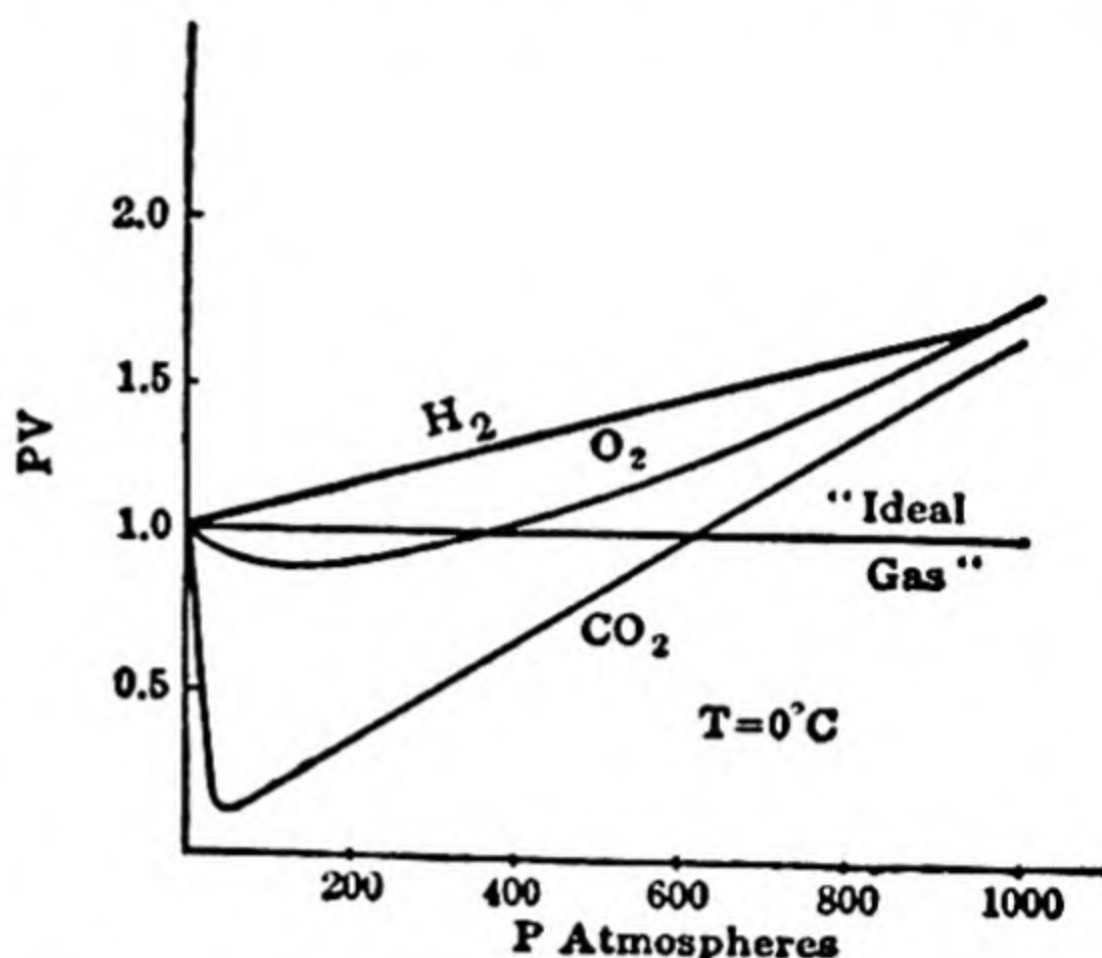
vessels. Liquids have no characteristic shape. Volume changes of liquids, resulting from changes in temperature and pressure, are small compared to those of gases. There are no general laws which describe the relation of the volume of liquids to temperature and pressure. When placed in separate layers in a vessel, liquids that are soluble in each other slowly diffuse to produce a solution of uniform composition. Under moderate pressures, liquids are much denser than gases.

These properties indicate that the molecules of liquids are much closer together and the forces of molecular attraction are much greater than in gases. One mole of water in the liquid state at its normal boiling point occupies a volume a little greater than 18 ml., but its volume in the gaseous state, at the same temperature and pressure, is approximately 31,000 ml. Although the molecules of liquids are in as rapid motion at any fixed temperature as the molecules of gases, the mean free path of the molecules of liquids is small.

Surface Tension. Beneath the surface of a liquid, a particular molecule is subject to attraction by other molecules around it. The forces are balanced in such a manner that the attraction is approximately equal in all directions. At the surface of the liquid, however, the forces of attraction are not uniform in all directions, and surface molecules are subject to a force that pulls them inward toward the center of the liquid. This force tends to cause a contraction in the surface area, making it as small as possible for the volume of the liquid. Work must be done to extend the surface of the liquid. The surface energy is measured as *surface tension*, which is the contractive force of the surface. It is this force that accounts for the spherical shape of falling drops of liquids, and for the rise of liquids in capillary tubes if they wet the walls of the tube. The surface tension of a liquid is affected by the presence of substances in solution and by the surface contact with other fluids in which the liquid is not soluble.

Viscosity. The attraction among the molecules of a liquid substance causes a greater viscosity than the molecular attraction in gases. *Viscosity* is the resistance shown by one portion of a liquid to flow over another portion. The tendency of a liquid to flow, the *fluidity*, is the reciprocal of the viscosity. The viscosity of a liquid

decreases with rise in temperature. The viscosities of different liquids vary greatly. Thus, gasoline has low viscosity and tar has high viscosity.

Vapor Pressure. The average kinetic energy of the molecules of a liquid is constant at fixed temperature, but some of the molecules have greater than average energies, so that they may break away from neighboring molecules. Thus, there is a continual escape of molecules into the space above the liquid. This process is *evaporation*. The gaseous molecules, formed by the evaporation of a liquid, constitute its vapor. Gaseous molecules also return to the liquid state, a process of *condensation*. If a liquid evaporates into a closed space, its gaseous molecules cannot leave the vicinity of the liquid surface, and the concentration of the gaseous molecules increases. This leads in turn to a corresponding increase in the rate of condensation. Evaporation of a liquid and condensation of its vapor are, therefore, opposite processes which take place in the same container. Ultimately the two changes become adjusted so that they continue at the same rate. The system is now in a state of equilibrium, and the space above the liquid is saturated because it contains

Fig. 23. *Vapor Pressure of Water* (20°)

the concentration of vapor required for equilibrium. *The vapor pressure of a liquid is the pressure exerted by its pure vapor in equilibrium with the pure liquid.* The vapor pressure of a liquid is affected by changes in temperature, and, to a small extent, by changes in the pressure of air on the liquid phase.

The vapor pressure of a liquid may be measured directly by introducing a few drops into the space above the mercury in a barometer tube. The liquid evaporates quickly to saturate this enclosed space, and the vapor causes a decrease in the height of the mercury column. At 20°, the pressure of saturated water vapor

is 17.5 mm. (Fig. 23.) Different liquids have different vapor pressures at the same temperature. Ether evaporates more rapidly than water and has a higher vapor pressure.

The Normal Boiling Point of a Liquid. The vapor pressure of a liquid increases with rise in temperature because the rate of evaporation increases, and a greater concentration of the vapor is required to establish equilibrium. The effect of temperature changes on the vapor pressure of a few liquids is shown in Fig. 24. Vapor pressures are the ordinates and temperatures are the abscissas of the curves. When a liquid is heated in a vessel open to air, the maximum pressure of the vapor is equal to the atmospheric pressure. Continued application of heat does not cause a further rise in temperature, but the rate of evaporation is increased and the
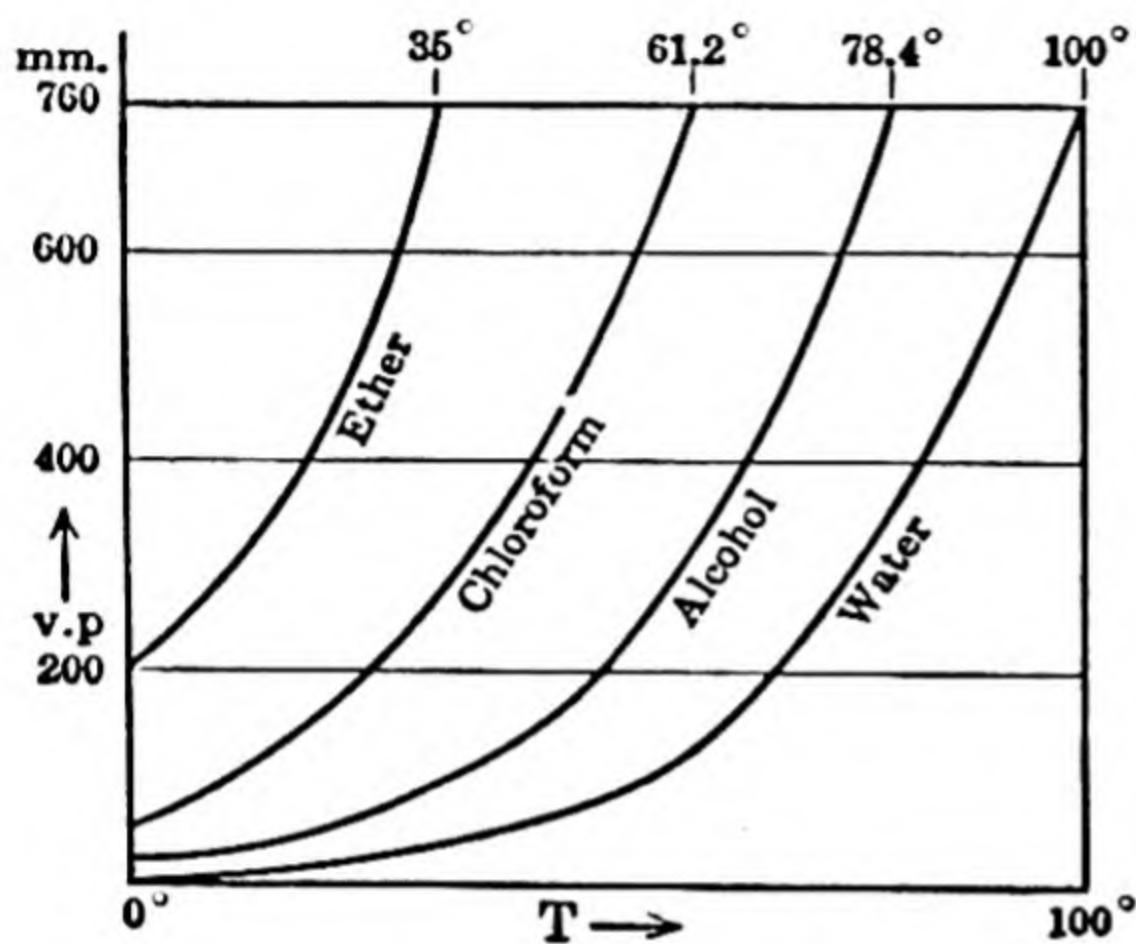
Fig. 24. *Vapor Pressure Curves*

liquid boils. The temperature required to boil a liquid in an open vessel depends on the nature of the liquid and the atmospheric pressure. Each liquid has a definite boiling temperature at a definite pressure. *The normal boiling point of a liquid is the temperature at which its vapor pressure is equal to one standard atmosphere, 760 mm.* The normal boiling point of water is 100°, but water may boil at other temperatures, *e.g.*, 90° at a pressure of 526 mm. The energy absorbed during the boiling of a liquid is expended in overcoming the attraction of the molecules for each other. The number of calories of heat required to convert a gram of a liquid at its boiling point to vapor at the same temperature is the *heat of vaporization* of the substance. The heat of vaporization of water is 540 calories per gram.

The Critical Temperature of a Substance. Critical temperature is defined as the highest temperature at which the liquid and gaseous phases of a substance may exist in equilibrium with each other. The maximum vapor pressure a liquid may exhibit is,

therefore, the vapor pressure at the critical temperature. This is called the critical pressure. The effect of changes in temperature on the vapor pressure of a liquid is greater at high than at low temperatures. The vapor pressure of water is 1 atmosphere at 100°; 15.34 atmospheres at 200°; 84.78 atmospheres at 300°; and 217.72 atmospheres at 374°, the critical temperature. The vapor pressure curve of water from 100° to its critical temperature is represented in Fig. 25. On the scale used in this figure, vapor pressures at temperatures below 100° are not distinguishable. These are shown in

Fig. 25. Vapor Pressure Curve of Water

Fig. 24, where the pressure unit is one millimeter of mercury instead of one atmosphere. The vapor pressure curve of a liquid terminates at the critical temperature, because only the gas phase can exist at higher temperatures.

In terms of the kinetic theory, the energy of molecules increases with rise in temperature, thus making the relative effect of molecular attraction less. The forces of attraction of the molecules may be increased by crowding them closer together, thus increasing the concentration. A balance between these two effects may be maintained and equilibrium may exist at temperatures below the critical temperature. At the critical temperature, however, the molecules have the maximum kinetic energy which they may possess and still exist in the liquid state in equilibrium with the gaseous form of the substance. At higher temperatures, the kinetic energy of the molecules is too great for condensation to occur, no matter how closely the particles are crowded together.

Liquefaction of Gases. A gas liquefies under conditions that give an actual vapor pressure greater than that of the saturated vapor of the substance. The concentration of the vapor must decrease in such systems in order to establish equilibrium. Consequently, a portion of the vapor liquefies. The liquefaction of a gas may be brought about by lowering the temperature to the necessary
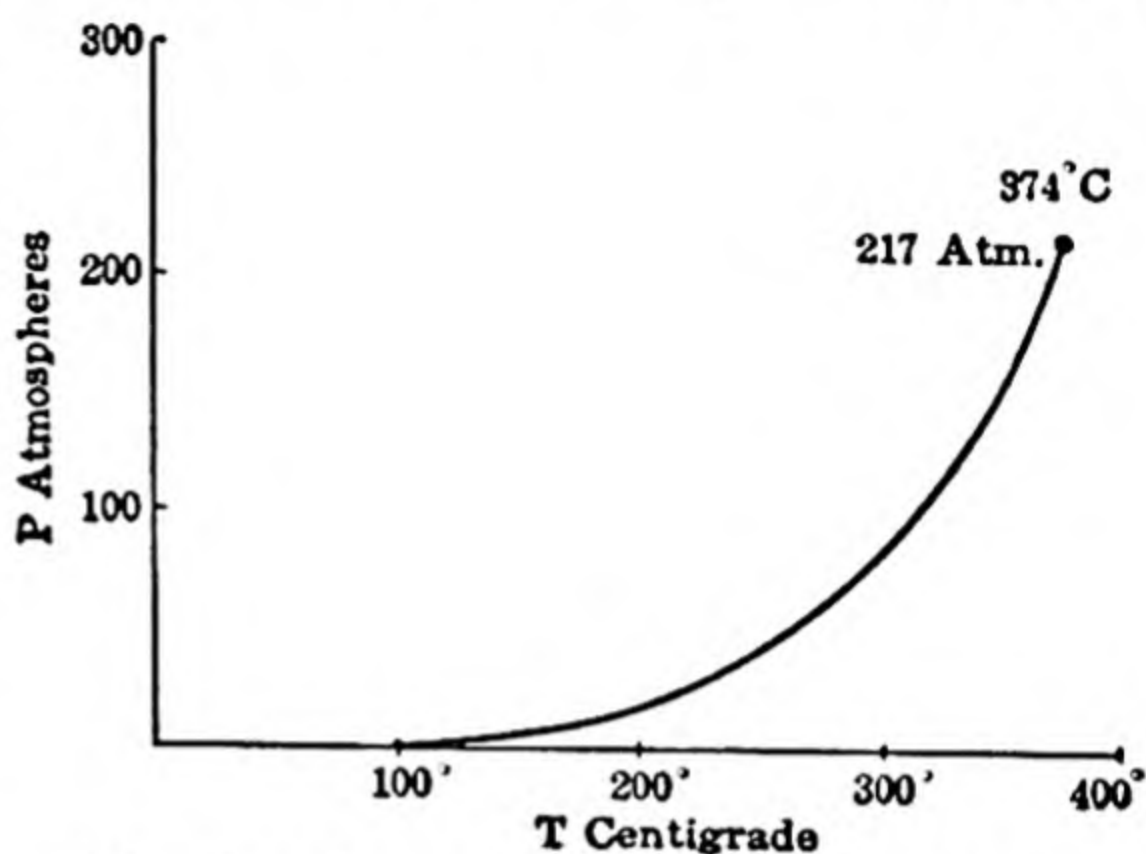
extent, by compressing the gas unless the temperature is above the critical temperature, and by combining these two effects.

The simplest method for the liquefaction of gases, if *transition temperatures are not too low* at normal pressures, is to cool the vapor. When the vapor is cooled to the boiling temperature of the substance at existing pressure, liquid is usually formed, although some substances pass directly from the gaseous to the solid state. Heat is evolved during the process of liquefaction. The heat of condensation is equal to the heat of vaporization of the same substance. The temperature required for the liquefaction of a gas may be raised by the application of pressure, but each gas must be cooled at least to the critical temperature to permit liquefaction.

The liquefaction of gaseous substances having moderately high critical temperatures, such as temperatures in the range covered by readily
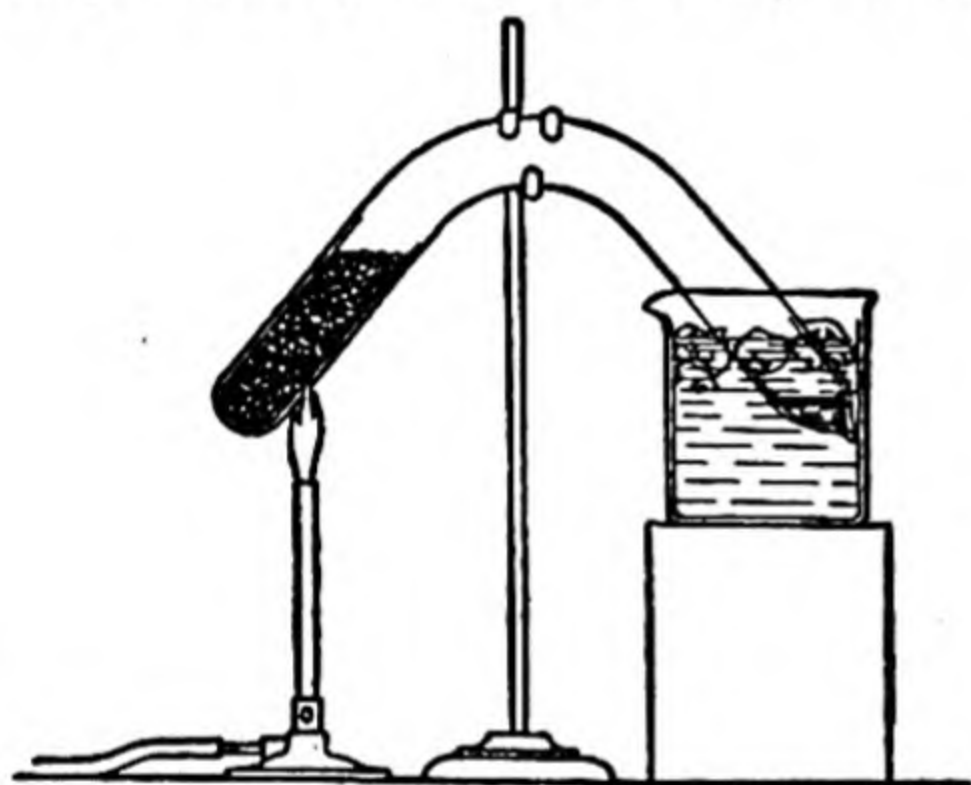
Fig. 26. *Liquefaction of a Gas*

available cooling agents, offers no experimental difficulties. Commonly, cold water, ice, and ice-salt mixtures are used for this purpose. In 1823, Faraday commenced a series of experiments liquefying many of the gases known at that time. The method consists in preparing the gaseous substance from solid materials placed in one end of a strong, bent glass tube, sealed at both ends. The other end of the tube is cooled by a suitable refrigerating material. (Fig. 26.) The gas, generated by heating the solid materials, develops enough pressure to cause liquefaction in the cold part of the tube. There are, however, a number of gases for which this method is not applicable.

The liquefaction of gases with low critical temperatures is more difficult because more efficient refrigerating materials are required. Solid carbon dioxide produces lower temperatures than may be obtained with ice, and liquid air gives still lower temperatures. The low temperature necessary for the liquefaction of many gaseous substances may be secured by application of the cooling effect produced by the expansion of the gas. If a highly compressed gas, composed of molecules with significant forces of attraction for each

other, is allowed to expand quickly to low pressure, its molecules overcome the forces of attraction at the expense of their own kinetic energy. Consequently, the temperature of the gas is lowered. When a gas expands without doing external work, the change in temperature is known as the *Joule-Thomson effect*. The cooling effect is greater for a gas at high pressure and low temperature than for the same substance under ordinary conditions, because of the greater effect of the forces of molecular attraction. This principle may be applied progressively by cooling the compressed gas to the temperature of the gas which has just expanded. This cool compressed gas is then allowed to expand, thus becoming still cooler. Ultimately, the gas may be cooled in this way to low enough temperatures to cause it to liquefy.

If at ordinary temperatures molecules of a gas exhibit no attraction, the Joule-Thomson effect is not applicable. Hydrogen and helium are gases of this nature. Consequently, it is necessary to cool these highly compressed gases to very low temperatures in order to produce a cooling effect by their expansion. This may be done through the use of liquid air.

Air may be liquefied by the application of the principle discussed in the preceding paragraph. An apparatus for this purpose was devised by Linde in 1895. Air, which has been dried and purified to remove carbon dioxide, is compressed under a pressure of approximately 200 atmospheres. The heat of compression is taken away by cooling with water. The compressed air now passes into the inner tube of the heat interchanger (Fig. 27), made of two concentric copper tubes closely coiled and packed in a heat-insulating material. Compressed air is released

Fig. 27. Heat Interchanger

through a needle valve at the lower end of this tube, and the pressure suddenly drops to approximately one atmosphere. The air, cooled by its expansion, passes out through the outer tube of the coil, thus cooling the incoming compressed air. After a time, the

temperature becomes low enough to cause a portion of the air to liquefy as it passes through the needle valve.

Containers for liquid air, known as Dewar flasks, are double-walled glass vessels. The space between the walls of the flask is evacuated to prevent conduction of heat to the contents. The inner surface of the outer tube may be silvered to prevent the absorption of radiant heat. Flasks made on this principle are familiar as thermos bottles.

The liquefaction of air is now of great industrial importance. When liquid air is distilled, different components predominate in the fractions obtained at varying temperatures. Commercial oxygen, nitrogen, argon, and neon are obtained by the liquefaction and fractionation of air. Liquid air also has important scientific uses as a refrigerant for securing low temperatures.
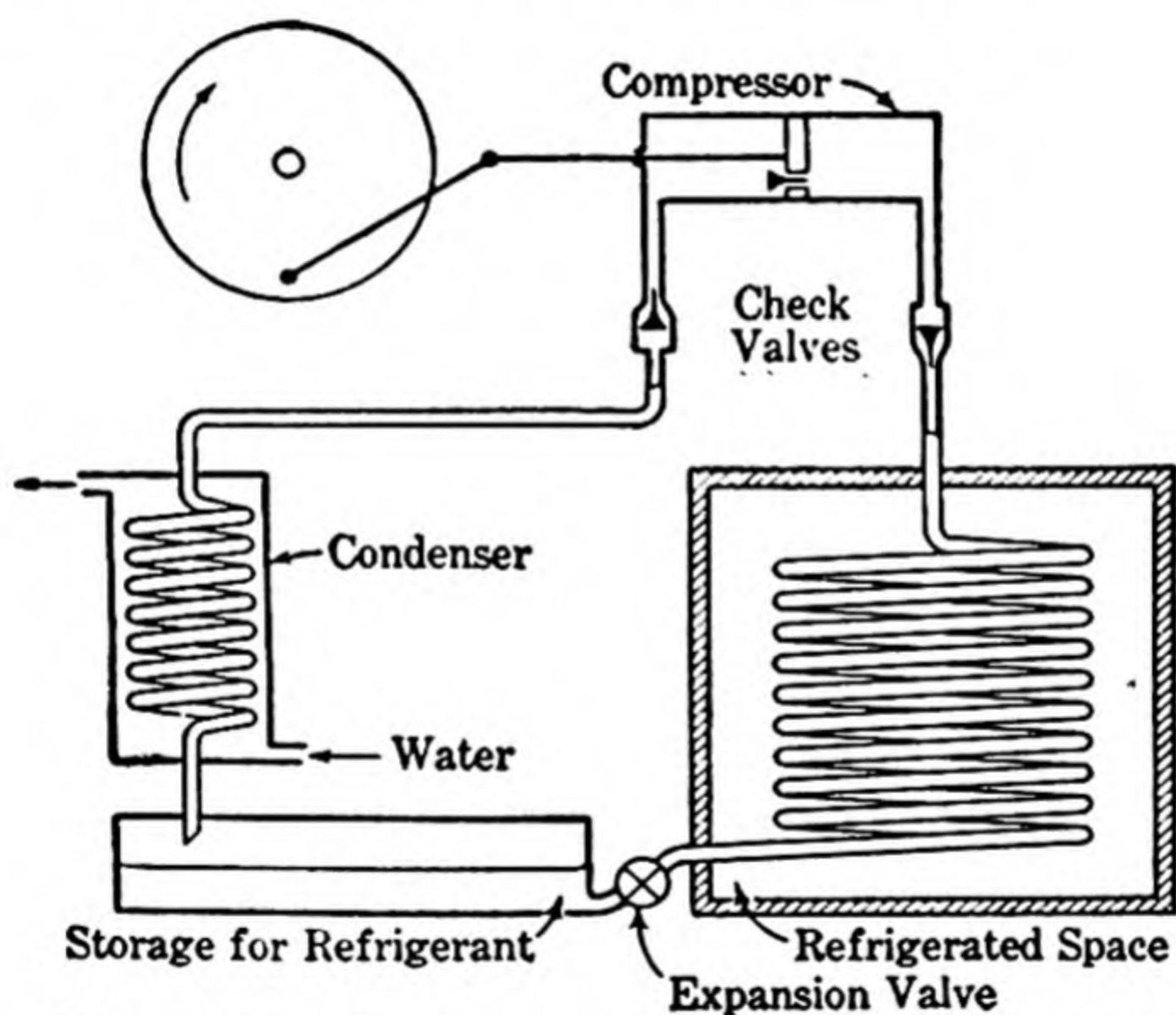
From " Chemistry in Refrigeration " by F. G. Keyes, Chemistry in Industry.
By permission of the author and Chemical Foundation, Inc.

Fig. 28. Compression Machine

Refrigerating Machines. An extensive application of the liquefaction of gases is in refrigeration. For use in refrigerating machines, a substance must have suitable freezing and boiling points, a high critical temperature, and a great vaporization heat. Ammonia, sulfur dioxide, methyl chloride, and difluorodichloromethane, Freon, have appropriate properties for such uses. The two types of re-

frigerating machines in common household use are compression
machine and absorption machine. The pressure required to liquefy
the gas in the condensing unit of a *compression machine* (Fig. 28) is
developed by a motor-driven pump. The condenser is usually air-
cooled. The liquid passes through an expansion valve in a coil in
the space to be refrigerated. Heat is absorbed during the evapora-
tion of the liquid. The condensation and evaporation processes are
intermittent and are controlled automatically. A brine around the
coil in which the evaporation takes place is cooled, and this brine
maintains the lowered temperature of the refrigerator during the
condensation stage of the cycle.

In the absorption machine (Fig. 29) the vapor of the refrigerant
is absorbed in a suitable material, and subsequently expelled from
this material by heat, so as to develop the pressures required for
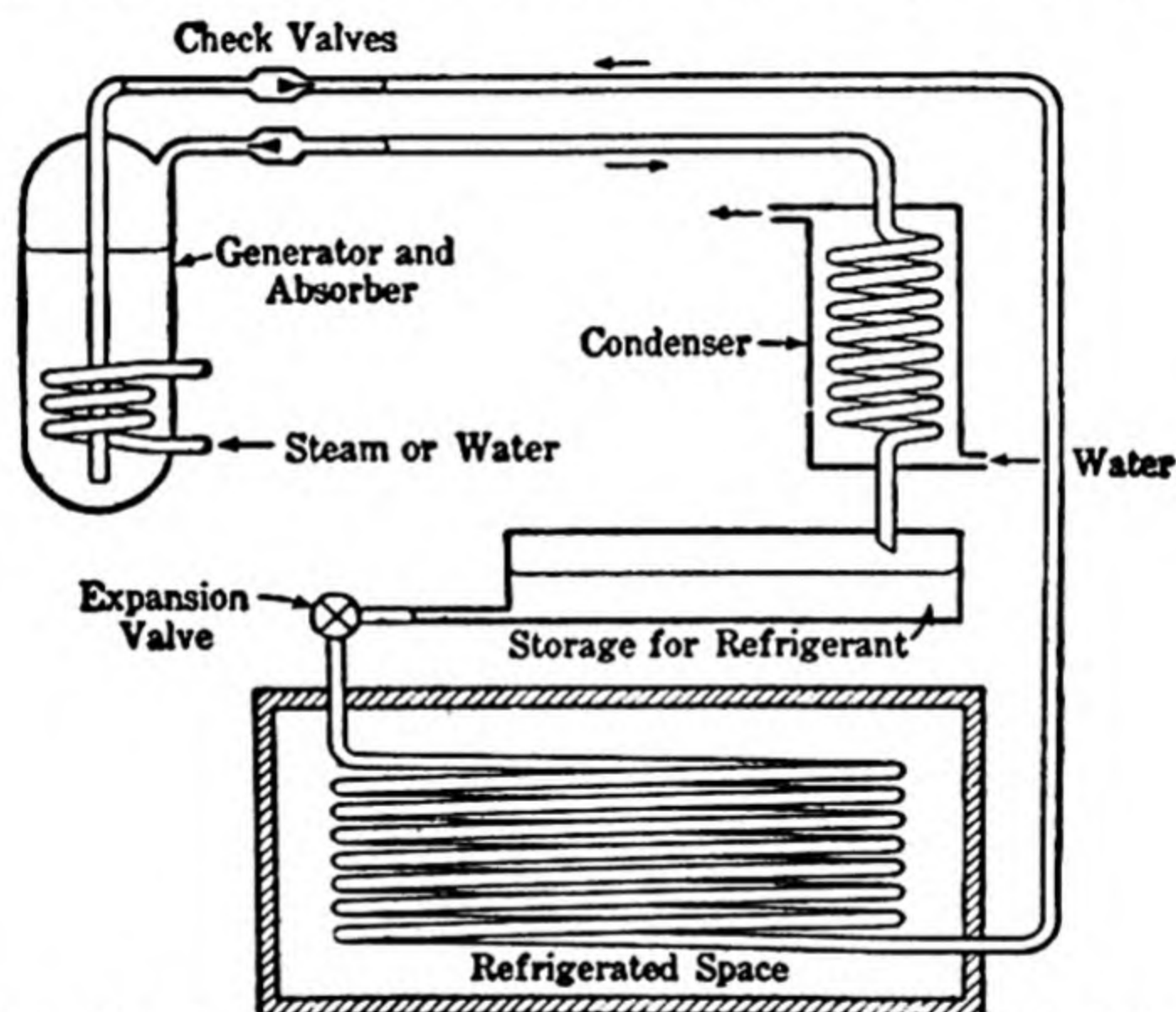
From "*Chemistry in Refrigeration*" by *F. G. Keyes*, Chemistry in Industry.
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Fig. 29. Absorption Machine

liquefaction. Calcium chloride absorbs relatively large volumes of
ammonia at room temperatures, and the pressure of ammonia gas
in equilibrium with this material is relatively low. Ammonia gas
is released by heating this product. During the refrigerating stage
of a machine using this system, liquid ammonia evaporates, cooling
a brine in the space to be refrigerated. The gaseous ammonia is

absorbed by calcium chloride in the absorber. During the con-
densation stage, ammonia gas is formed again by heating the
material in the absorber so that it now becomes a generator. The
pressure developed is high enough to liquefy ammonia. When
most of the ammonia has condensed, the heating is discontinued,
and the absorbent is allowed to cool. The stages of the process are
repeated automatically.

THE SOLID STATE

A sample of a solid has definite volume, and is but slightly
affected by changes in pressure. The particles of the solid are close
together, and the forces of attraction give it varying degrees of
rigidity and mechanical strength. An orderly arrangement of the
particles gives a definite crystalline structure, which is characteristic
of the substance. The motion of the particles in the crystal is a
vibratory motion about a fixed position.

The Melting Point of a Solid. Under constant atmospheric
pressure, a crystalline solid melts at a definite temperature. So long
as the solid and liquid phases of a substance are together in an
intimate mixture, the temperature remains constant. *The tempera-
ture at which the solid and liquid phases of a substance are in equilibrium
under a pressure of one atmosphere is the melting point of the substance.*
The absorption of heat by a mixture such as this disturbs the
equilibrium, increasing the proportion of the liquid. The number
of calories of heat required to melt one gram of a solid at its melting
point is defined as the *heat of fusion.* The heat of fusion of water is
80 calories per gram.

The changes that take place during the freezing of a liquid are
opposite to those that take place during the melting of the solid.
The liquid freezes completely at a specific temperature, the melt-
ing point of the solid. Heat is evolved during the freezing of a
liquid. It is frequently possible to supercool a liquid to some tem-
perature below the normal freezing point without producing the
solid. But the addition of a crystal of the solid to the supercooled
liquid causes rapid crystallization; and the temperature remains
constant at the freezing point until solidification is complete.

Many crystalline substances have appreciable vapor pressures

at ordinary temperatures, and the vapor pressure of the solid increases with rise in temperature. A solid shows its maximum vapor pressure at the melting point, and a liquid in contact with the solid phase shows its lowest vapor pressure at the freezing point. The melting point of the solid and the freezing point of the liquid are the same. The two phases exist in equilibrium at this temperature, and therefore it is evident that they have the same vapor pressure. The relation of vapor pressure and temperature is shown for water by the curves in Fig. 30. The curve *AB* shows the effect of rising temperatures on the vapor pressure of ice. The curve *BD*, not drawn to scale, is the vapor pressure curve of water. The point *B*, where these curves intersect, represents the melting point at which the solid and
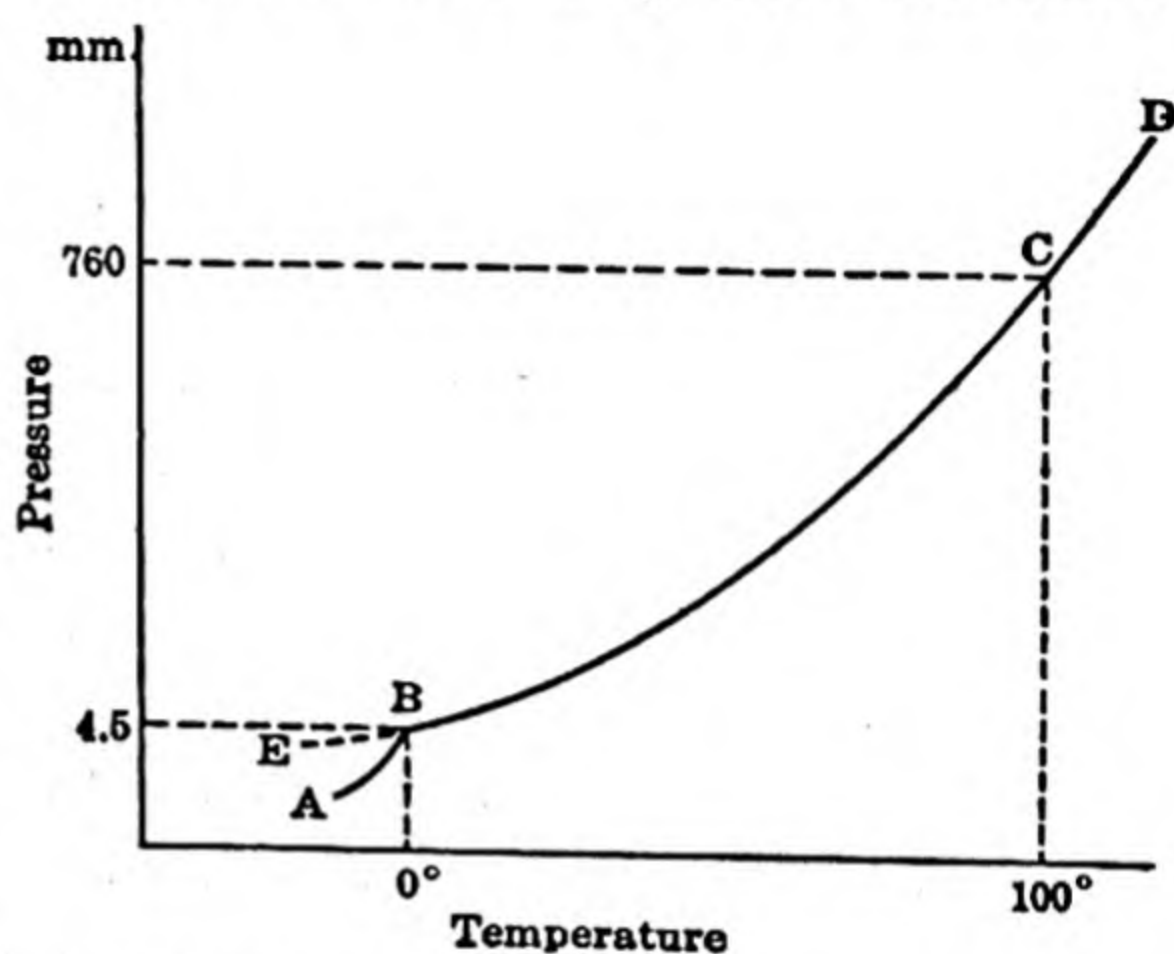
Fig. 30. *Vapor Pressure Curve of Water*

the liquid are in equilibrium and the vapor pressure of each is almost exactly the same, 4.6 mm. The temperature at which ice and air-saturated water are in equilibrium at one atmosphere total pressure is defined as 0°. The temperature at which ice, pure water, and pure vapor are in equilibrium, known as the *triple point* for water, is slightly above 0°, because the effects of air pressure and solution of air in water are removed. The point *C* represents the boiling point of water. The curve *BE*, an extension of the regular curve *BD* to temperatures below 0°, is the vapor pressure curve of supercooled water. The vapor pressure of this unstable phase is greater than that of the stable phase at the same temperature.

Sublimation of Solids. Some solids have high vapor pressures at ordinary temperatures and evaporate completely without melting, when they are heated. This phenomenon is called sublimation. Solid carbon dioxide, dry ice, has a vapor pressure greater than one atmosphere at any temperature above — 78.5°. Hence, except under high pressures, this substance cannot be kept in the liquid state, for equilibrium is impossible at a pressure of one atmosphere.

If the liquid is poured from a cylinder, it evaporates so rapidly upon emerging that a large proportion is cooled to form solid carbon dioxide snow. The vapor pressure of carbon dioxide at 20° is 56.5 atmospheres. The substance has no true melting point, and the solid sublimes when it is exposed at a pressure of one atmosphere.

The behavior of iodine is intermediate between carbon dioxide and water. The solid has moderate vapor pressure at room temperature and it evaporates rapidly. The vapor may be condensed directly to form the solid, known as a sublimate. If, however, the vapor pressure of iodine is kept to at least 100 mm., the solid may be melted.

Crystal Structure of Solids. A crystal has definite geometrical form and is bounded by plane faces. The size and external shape of the crystal of a given substance may vary, but the angle between two corresponding faces is the same in the stable form at a specified temperature. The geometrical form of a crystal depends on the arrangement of the particles throughout the crystal. The relative positions of the particles cannot be determined by examination under ordinary light, because light waves are not appreciably affected by such minute particles. The wave lengths of X-rays, however, are so much shorter that they are affected by the minute particles in the crystal. Investigations of these effects — made by Laue, W. H. Bragg, W. L. Bragg, and many others — have provided techniques for determining the relative positions of crystal particles.

The positions of the particles in the crystal determine the framework, known as the *crystal lattice*, on which the crystal is built. The smallest unit of this lattice, representing the relative positions of all of the particles, is known as the *unit cell*. The structure and the size of the unit cell are characteristic of each crystalline substance. *The structural particles*, which occupy or vibrate about the fixed positions in the crystal lattice, may be ions, atoms, or molecules. *Ions are atoms or radicals that bear electric charges.* The structural units in salts are positively and negatively charged ions, held in position by the forces of electrical attraction. The unit particles in the metals, and in some of the nonmetals, are atoms. The structural unit in many of the crystalline compounds other than salts is the molecule.

Crystal Systems. There are a large number of crystal forms, but these may be grouped into six systems based on the position of the facets in relation to definite axes. The position of the facet of a crystal can be determined by its points of intersection with three axes. The characteristic relations of these axes are shown in Fig. 31.

1. Cubic   2. Tetragonal   3. Hexagonal

4. Rhombic   5. Monoclinic   6. Triclinic
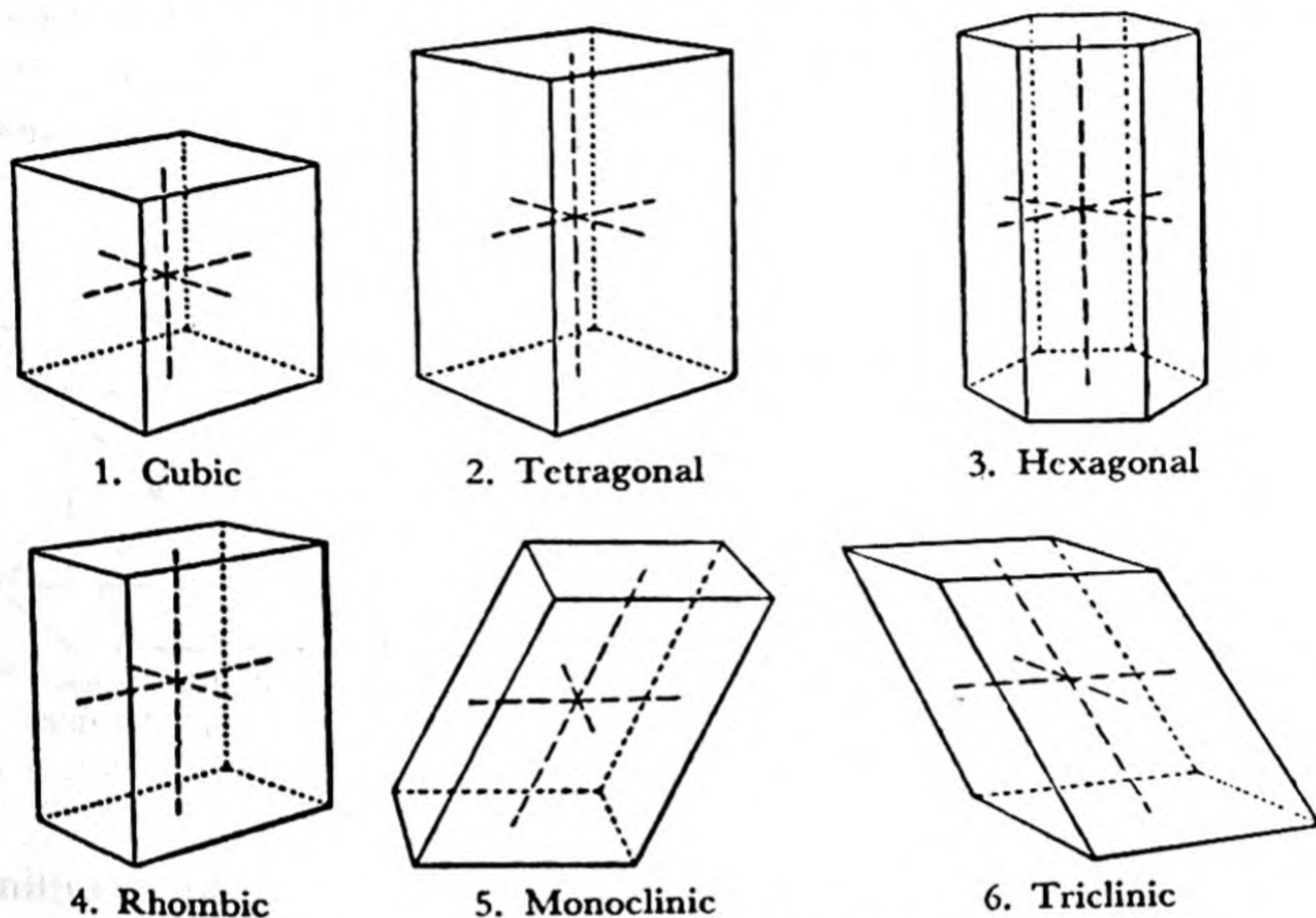
Fig. 31. Crystal Systems

The isometric or *cubic system,* three axes of equal length intersecting each other at right angles.

The tetragonal system, two axes of equal length intersecting each other and a third axis, either shorter or longer, at right angles.

The hexagonal system, three axes of equal length in the same plane, intersecting each other at an angle of 60°, and a fourth axis of different length perpendicular to this plane.

The rhombic system, three axes of unequal length intersecting each other at right angles.

The monoclinic system, three axes of unequal length, two intersecting each other at right angles, with the third axis perpendicular to only one of the two.

The triclinic system, three axes of unequal length intersecting each other at oblique angles.

The cubic system is the simplest of these classes of crystals, but there are three different space lattices in this system. (Fig. 32.) In the simple cubic lattice, one structural unit is at each corner of the cube. In the face-centered lattice, one unit is at each corner and one in the center of each facet of the cube. In the body-centered cubic lattice, one unit is at each corner and one in the center of the cube. Sodium chloride crystallizes in the simple cubic lattice. The structural units are positively charged sodium ions and negatively charged chloride ions, which occupy alternate corners in the cubic lattice.
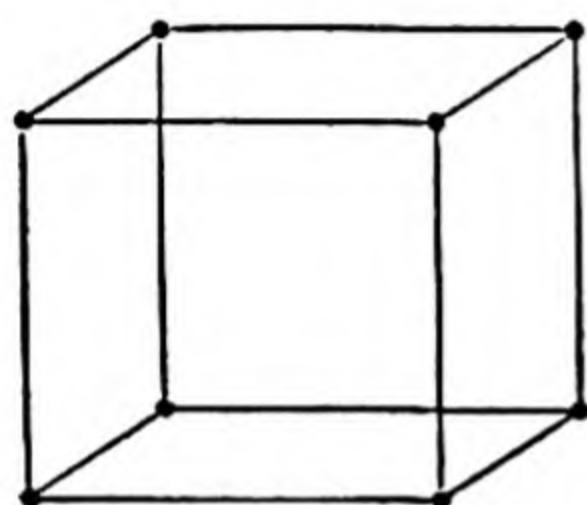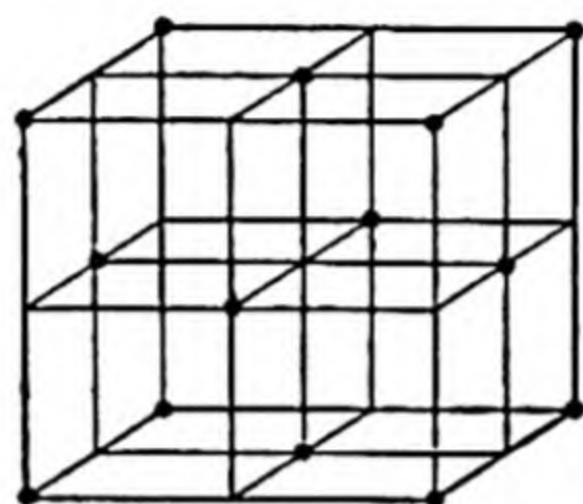
| Simple Cubic Lattice | Face-centered Cubic Lattice | Body-centered Cubic Lattice |
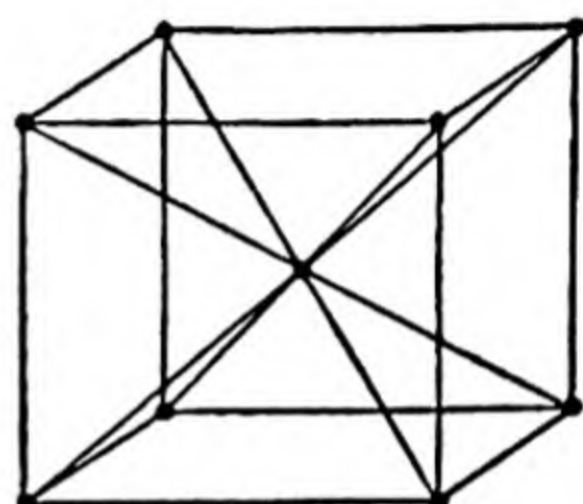
Fig. 32. Cubic Crystal System

Amorphous Solids. Amorphous materials are noncrystalline. Some of these materials possess the strength and hardness ascribed to solids, while others are softer and have little strength. An amorphous solid gradually softens when it is heated, but has no specific melting point or heat of fusion. The attractive forces of the structural units in an amorphous solid are exerted equally in all directions, and result in a random arrangement without symmetry. Structurally such substances are liquids having high viscosity. They are known as *supercooled liquids*. Many materials which may appear to be amorphous, such as finely divided powders, are really crystalline in structure, but the particles are so small that the structure is not apparent.

EXERCISES

1. State the fundamental assumptions of the kinetic theory, dealing with matter in the gaseous state. Show how these assumptions may be used to account for the compression, expansion, diffusion, and pressure exhibited by gases.
2. Explain in terms of the postulates of the kinetic theory the quantitative rela-

tionships between pressure, volume, temperature, and concentration of gases, as stated in the gas laws.

3. What two deviations from the gas laws are noted in the actual behavior of gases under increasing pressure? What is the cause of each of these deviations? What is the meaning of the expression "perfect gas"?

4. Compare the general properties of liquids with those of gases. How are these differences explained in terms of the kinetic theory?

5. Give an accurate statement of the meaning of the following: viscosity, surface tension, vapor pressure, boiling point, heat of vaporization.

6. What is a transition point? What conditions affect the transition temperature between the liquid and the gaseous forms of a substance?

7. What is meant by the critical temperature of a substance? In terms of the kinetic theory, account for the fact that there is a critical temperature of a substance, and that it differs for different substances.

8. What condition is prerequisite to the liquefaction of a gas? How is this condition established for (a) substances with relatively high critical temperatures, (b) substances with moderately low critical temperatures, (c) substances with very low critical temperatures?

9. Explain the application of the liquefaction of gases in refrigeration.

10. Compare the general properties of solids with those of liquids and of gases, and account for the differences.

11. What is the melting point of a substance? What is the vapor pressure relationship between the two phases at this transition temperature?

12. Explain the sublimation of a solid.

13. What factors determine the form of a crystalline solid? What is meant by the space lattice of a crystal? the unit cell?

14. Name three structural units of which crystals are composed, and give examples of each.

15. What are the differences between crystalline and amorphous substances?

SUPPLEMENTARY READINGS

Dampier-Whetham, W. C. D., *A History of Science*, The Macmillan Company, New York, 1930, pp. 248–53.

Moore, F. J., *History of Chemistry*, McGraw-Hill Book Company, Inc., New York, 1939, chap. IV.

Getman, F. H., and F. Daniels, *Outlines of Theoretical Chemistry*, John Wiley & Sons, Inc., New York, 1943, chaps. II–III.

Hildebrand, J. H., *Principles of Chemistry*, The Macmillan Company, New York, 1940, chap. III.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, American Book Company, New York, 1936, chap. III.

Stillwell, C. W., "Crystal Chemistry," *J. Chem. Education* **10**, 590, 637 (1933); **11**, 159 (1934); **13**, 415, 469, 521, 566 (1936); **14**, 34, 131 (1937).

Chapter 6

HYDROGEN. WATER

In the sixteenth century, Paracelsus observed the formation of a gaseous product in the reaction of sulfuric acid with iron. He concluded that this gas was air, because air was the only gas known at that time. In the latter part of the sixteenth century, Boyle collected a sample of this gas and observed its combustibility. Cavendish (1731–1810) investigated the properties of the gas and recognized its elementary nature. He also determined that the combustion of hydrogen yields water. The name, hydrogen, meaning water former, was first used by Lavoisier.

Occurrence of Hydrogen. Approximately one per cent, by weight, of the matter in the outer part of the earth and its atmosphere is hydrogen. This element is a constituent of a large number of compounds, but only an insignificantly small percentage of free hydrogen is found in the air. The most abundant of the compounds of hydrogen is water, which contains approximately 11 per cent of hydrogen. Organic matter contains hydrogen, and acids and hydroxides of metals are hydrogen compounds. Hydrogen compounds are abundant, but the small percentage of free hydrogen is due to its low atomic weight. On the basis of relative numbers of atoms, hydrogen ranks next to oxygen among the elements in the outer part of the earth.

Reactions Producing Hydrogen. There are a number of reactions that result in the production of elementary hydrogen. The displacement of hydrogen from some of the acids by the action of metals has been discussed in Chapter 4, page 59. Water may be decomposed into elementary hydrogen and oxygen by a direct current of electricity. Several of the metals are active enough to displace hydrogen from water, *e.g.*, potassium, calcium, and sodium. The hydroxide of the metal is the product of this reaction.

$$Ca + 2 H_2O \longrightarrow H_2 + Ca(OH)_2$$
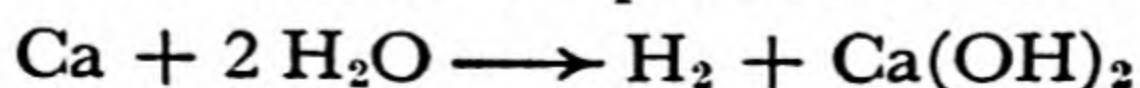
Aluminum and magnesium usually become protected with a surface film so that they do not react readily with water unless this surface film is removed.

Some of the metals, not active enough to react with water at ordinary temperatures, do react at high temperatures. When steam is passed into a tube containing finely divided iron heated to a high temperature (Fig. 33), hydrogen and iron oxide are
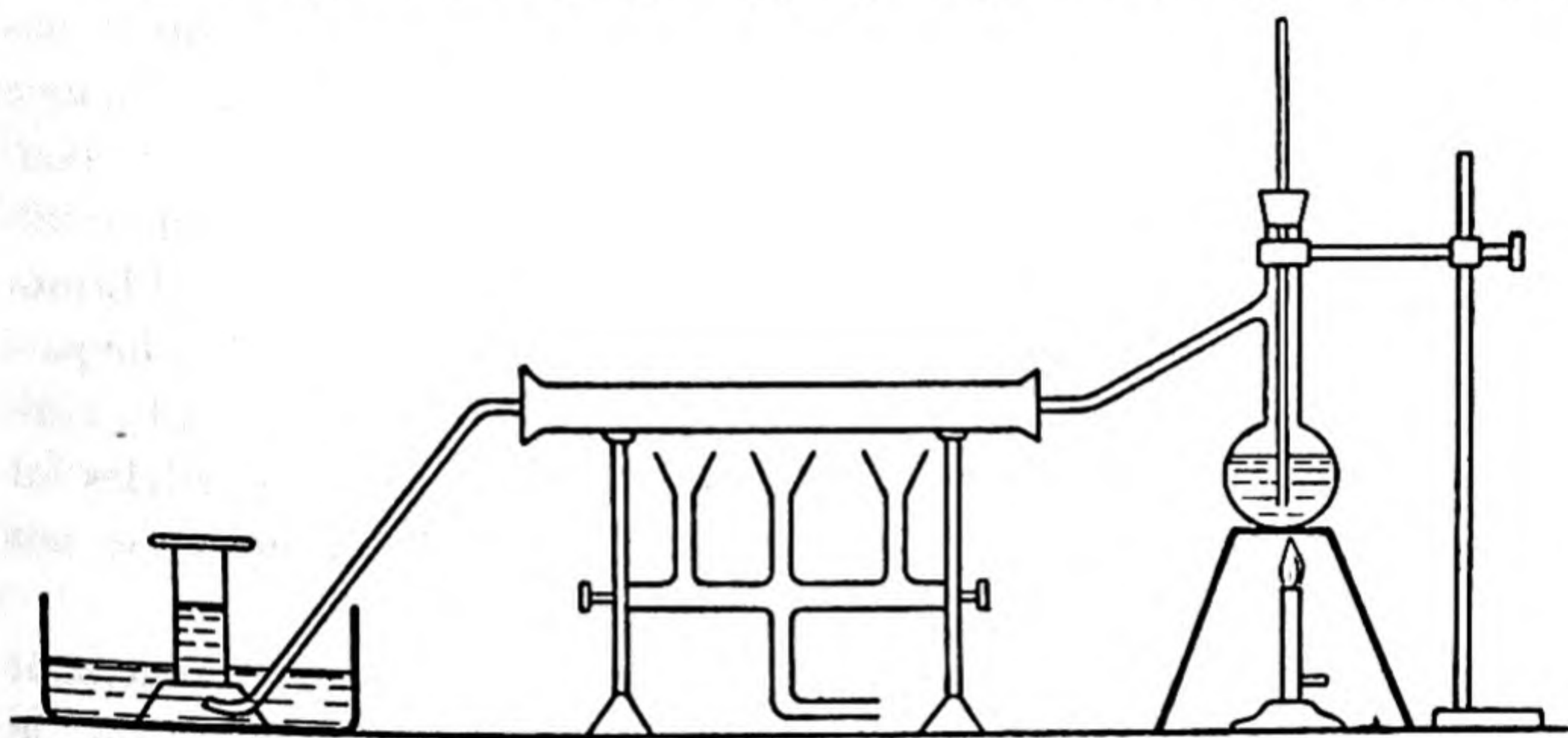
Fig. 33. Reaction of Steam with Iron

produced. The compound known as the magnetic oxide of iron, Fe_3O_4, is the usual product of the reaction of steam with iron.

$$3\,Fe + 4\,H_2O \longrightarrow 4\,H_2 + Fe_3O_4$$
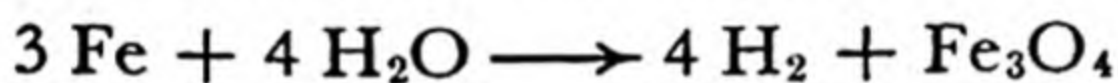
Steam also reacts with carbon at a temperature of about 1000° to form hydrogen and carbon monoxide.

$$C + H_2O \longrightarrow H_2 + CO$$
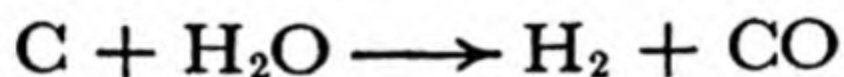
Reversible Reactions. The reaction of steam with hot iron is reversible. The products of a reversible reaction interact to form the initial substances. So long as all of the reacting materials remain together in a closed system under conditions required for reaction, both changes continue. If one of the reactions proceeds more rapidly than the other, the concentrations of the reactants are altered in such a manner as to reduce the velocity of this reaction and to increase the velocity of the opposite reaction. Consequently, the concentrations become adjusted so that the two attain the same velocity.

$$3\,Fe + 4\,H_2O \rightleftharpoons 4\,H_2 + Fe_3O_4$$
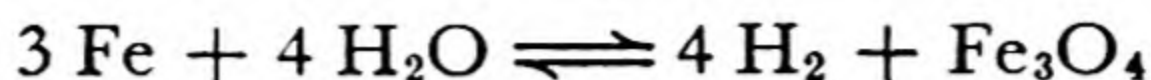
A system is in a state of equilibrium when the two reactions it involves proceed with the same velocity. A change affecting the velocity of one of two reactions of opposite effect more than the other causes a change in the concentrations of the reacting substances, and thus maintains the ratio necessary for equilibrium. If a change in conditions causes the continuous elimination of materials from the system, equilibrium cannot be established. The passage of steam into the tube containing fine iron particles at high temperature (Fig. 33), with the removal of hydrogen, does not cause equilibrium.
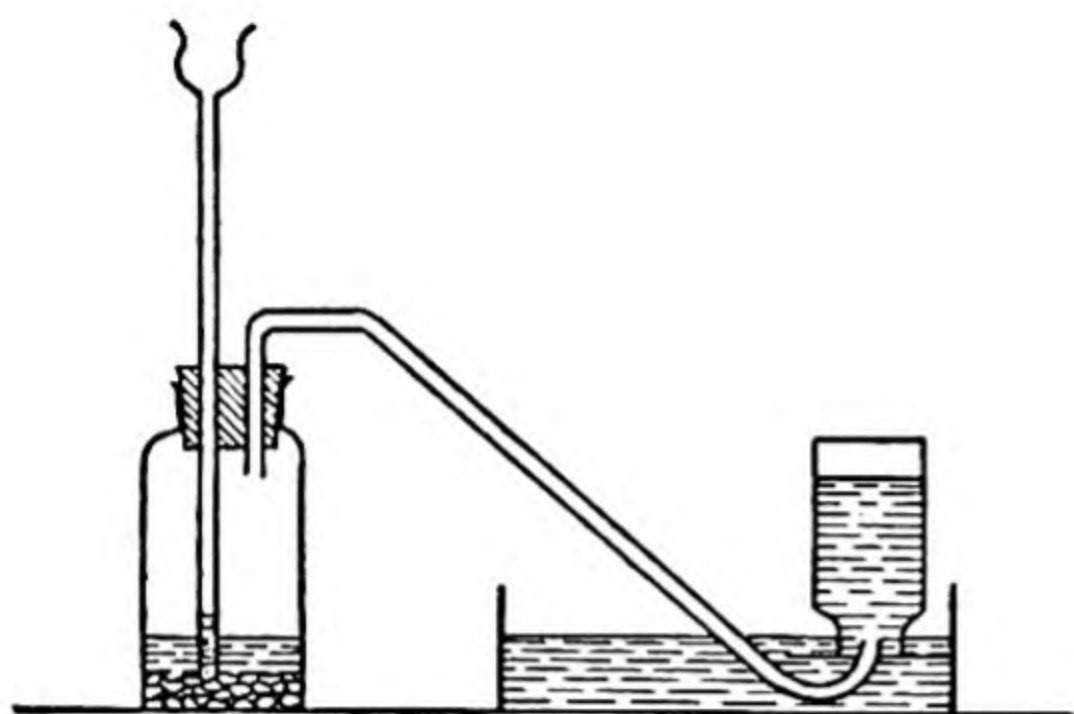
Fig. 34. *Laboratory Preparation of Hydrogen*

Laboratory Preparation of Hydrogen. The most convenient laboratory method for the preparation of hydrogen is based on the reaction of zinc with dilute sulfuric acid. The gas is collected over water. (Fig. 34.) Other metals could be selected, but some react too violently and others too slowly. Zinc's rate of reaction can be easily controlled by regulating the rate with which sulfuric acid is added.

$$Zn + H_2SO_4 \longrightarrow H_2 + ZnSO_4$$
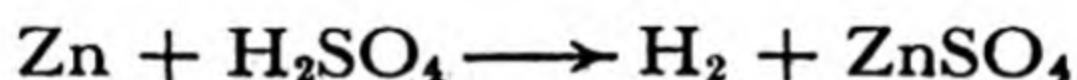
A small quantity of copper sulfate solution is usually introduced into the generator bottle. Zinc displaces copper from this solution, thus providing contact between zinc and a metal of lower activity.

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$$
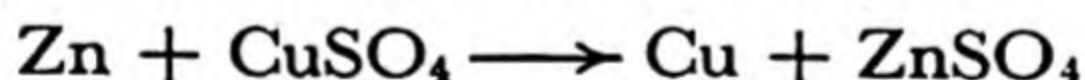
The reaction of zinc with the acid proceeds more rapidly under these conditions than when pure zinc is used. The surface of pure zinc, placed in a solution of dilute sulfuric acid, becomes coated with a film of hydrogen, and the reaction proceeds so slowly that the evolution of gaseous hydrogen cannot be observed. When zinc is in contact with a metal of lower activity, hydrogen is evolved at the surface of this less active metal. Thus, a fresh surface of zinc is constantly exposed to the action of the acid.

A convenient apparatus for the preparation of hydrogen in laboratory practice is the Kipp generator. (Fig. 35.) Zinc rods are placed in the middle compartment of this generator, and the acid is poured in at the top until the lower compartment is filled and the upper is about half full. When the stopcock is opened, the acid rises into the middle compartment in contact with zinc. Hydrogen, produced by the reaction, passes out through the delivery tube. When the stopcock is closed, hydrogen accumulates and develops a pressure that forces the acid down and away from the zinc, the excess rising into the upper compartment. Zinc is now out of contact with the acid and the reaction ceases.

Fig. 35. Kipp Generator

Industrial Preparation of Hydrogen. The production of hydrogen in the quantities required for industrial processes is accomplished by the decomposition of natural compounds. The most important methods of producing commercial hydrogen are based on the reaction of water with hot carbon, the decomposition of water by electric current, the decomposition of methane, and the decomposition of complex compounds in soft coal.

In the water-gas method of hydrogen production, steam is passed over coke at approximately 1000°, forming a mixture of hydrogen and carbon monoxide, known as *water gas*. The reaction is endothermic and, consequently, the temperature drops until it is too low for rapid reaction. Steam is then cut off, and air is admitted under forced draft, burning coke until it is white hot. Carbon dioxide formed in this stage is a waste product. The air draft is then shut off, and steam is again passed through the hot coke. The process continues intermittently.

$$C + H_2O \longrightarrow H_2 + CO - 28,300 \text{ cal.}$$
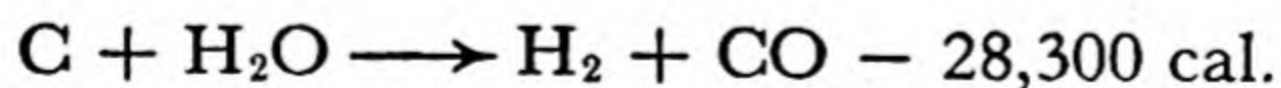
In a second step in the procedure, an excess of steam is introduced into the mixture of hydrogen and carbon monoxide, and the gases are passed in contact with a catalyst, consisting of iron oxide with small proportions of oxides of nickel and chromium, at
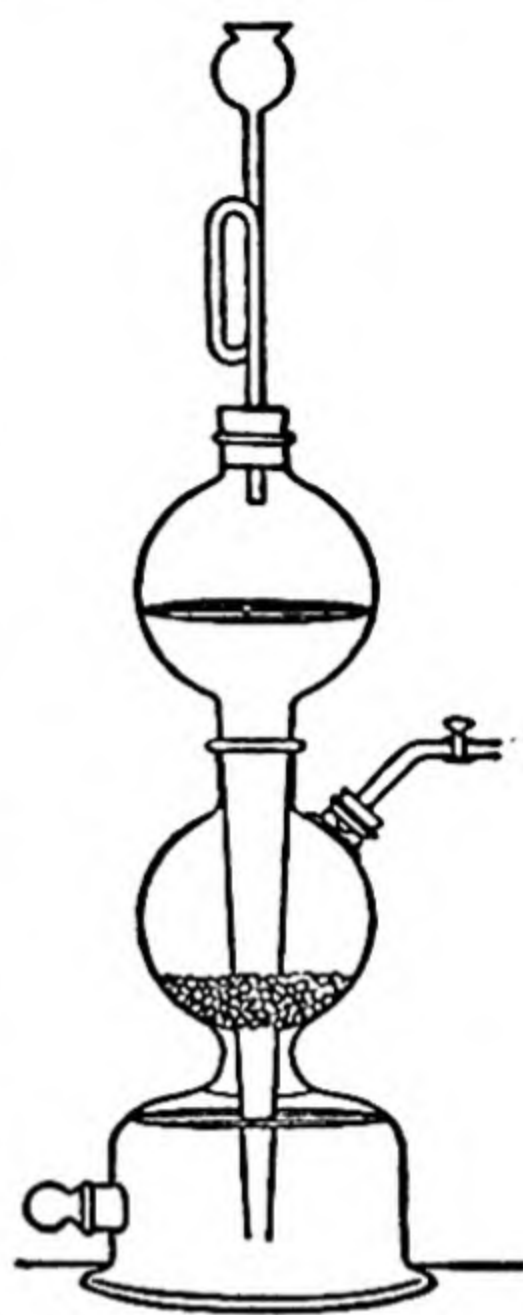
500°. The reaction produces hydrogen and carbon dioxide. This reaction is exothermic and reversible. Consequently, some carbon monoxide is always present among the products.

$$CO + H_2O \rightleftharpoons H_2 + CO_2 + 9800 \text{ cal.}$$
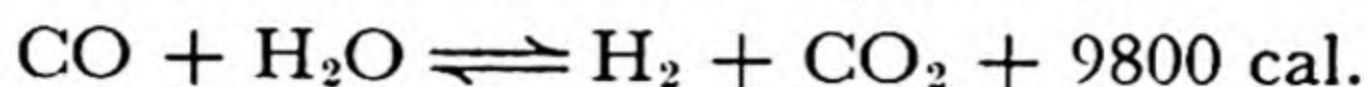
Carbon monoxide is the more stable product at the higher temperatures and carbon dioxide at temperatures below 500°. Most of the carbon dioxide is absorbed by passing the gas mixture under pressure into water. The remainder is taken out by reaction with sodium hydroxide or calcium hydroxide.

$$CO_2 + 2\,NaOH \longrightarrow H_2O + Na_2CO_3$$
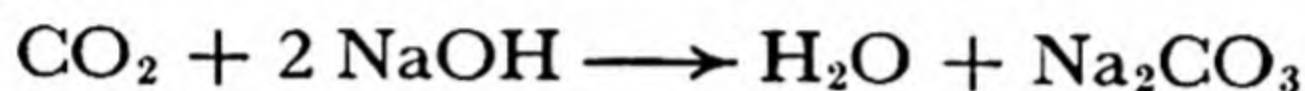
To remove the carbon monoxide remaining in the gas, the correct proportion of oxygen is introduced to oxidize it to carbon dioxide, and the mixture is passed in contact with a second oxide catalyst.

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$
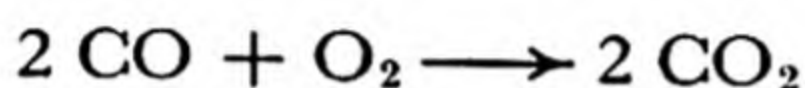
Carbon dioxide formed in this step is removed as above.

The electrolysis of water is the process of decomposing the compound into its constituent elements by means of a direct current of electricity. Sodium hydroxide is dissolved in water to provide a conducting solution. Hydrogen is discharged at the negative electrode, the cathode, and oxygen at the positive electrode, the anode. The electrolysis of a sodium chloride solution produces hydrogen and sodium hydroxide at the cathode and chlorine at the anode.

The reaction of methane with steam at high temperature, in the presence of special catalysts, is an important process for the production of hydrogen. Carbon monoxide — a product of the first reaction — may be caused to react with steam, as discussed in the preceding paragraph.

Destructive distillation is the decomposition of a complex substance by heat, accompanied by the volatilization of products having low boiling points. The destructive distillation of soft coal produces a gaseous product known as coal gas, a complex liquid mixture called coal tar, and a solid residue known as coke. Approximately 50 per cent of the gaseous mixture is hydrogen and 30–35 per cent methane. Hydrogen gas may be secured from this mixture by the liquefaction of the other components, or the hydrocarbons may be converted into hydrogen and carbon dioxide, as indicated above.

Properties of Hydrogen. The gas is colorless, odorless, and tasteless, and is very slightly soluble in water. It has the least density of all substances. One liter weighs 0.0899 g. at 0° and 760 mm. Hydrogen diffuses more rapidly than any other gas. An effect of its rapid diffusion may be shown by placing a jar of hydrogen over a porous earthenware cup containing air at atmospheric pressure, arranged as shown in Fig. 36. Molecules of hydrogen pass through the pores into the cup so much faster than molecules of oxygen and nitrogen pass out that a pressure is created and water is driven out the side tube. Relatively large volumes of hydrogen are absorbed by some metals. Finely divided iron absorbs approximately 20 times its volume, and palladium approximately 800 times its volume of hydrogen, at 20° and a gas pressure equal to one atmosphere. The boiling point of liquid hydrogen is − 252.8°, the freezing point − 259.2°, the critical temperature − 240°, and the critical pressure 12.8 atmospheres.
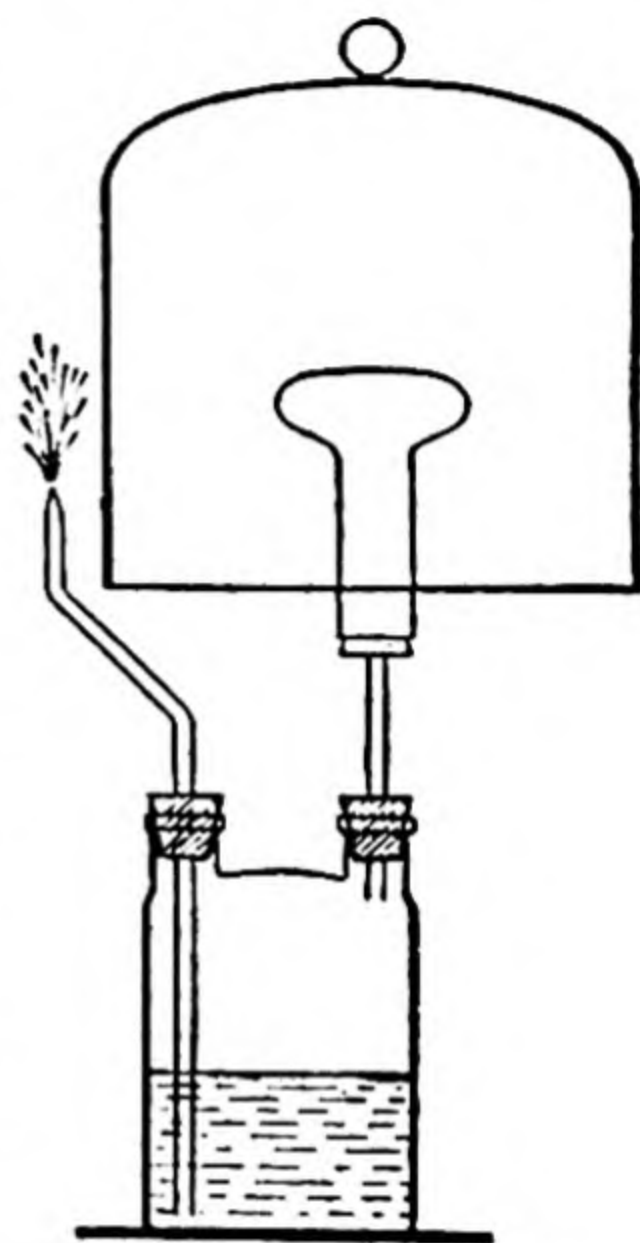
Fig. 36. Hydrogen Diffusion Fountain

Reactions of Hydrogen. Hydrogen reacts with a number of the nonmetals to form hydrides. These reactions have been illustrated previously as examples of the direct union of elements on page 55. Hydrogen unites also with some of the metals, but metal hydrides are, in general, not stable toward heat. Hydrogen reacts with the oxides of a number of metals to form water and free metal.

$$CuO + H_2 \longrightarrow H_2O + Cu$$
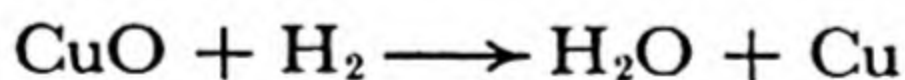
Hydrogen reacts with carbon monoxide at high pressure in contact with a zinc catalyst, forming methanol, CH_3OH.

$$CO + 2 H_2 \rightleftharpoons CH_3OH$$
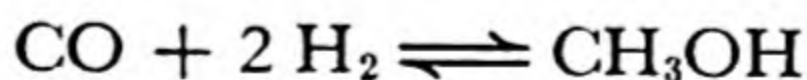
Many compounds containing relatively small percentages of hydrogen combine with additional hydrogen. The compounds which react in this manner are called *unsaturated compounds*. There are a number of unsaturated hydrocarbons and other substances

derived from the hydrocarbons. The combination of these unsatu-rated substances with hydrogen is an *addition reaction*. The hydro-carbon, ethylene C_2H_4, combines with hydrogen in the presence of a platinum catalyst to form ethane, C_2H_6.

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$
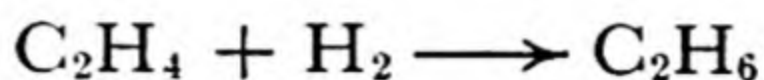
Deuterium. In 1931, Urey, Murphy, and Brickwedde announced the discovery of a variety of hydrogen with an atomic weight almost double that of ordinary hydrogen. Heavy hydrogen is now called *deuterium*. The chemical reactions of these two varieties of atoms are almost identical, but the physical properties differ. The density of gaseous deuterium is double that of hydrogen; the boil-ing point of the liquid is − 249.5° and the freezing point − 254.3°. Two varieties of atoms with similar chemical properties but dif-ferent atomic weights are called *isotopes*. An explanation of these differences is given in Chapter 13.

Industrial Uses of Hydrogen. On account of its low density, hydrogen has been used extensively in balloons and dirigibles, but its combustibility has resulted in a number of disastrous ex-plosions and fires, causing the total destruction of the airship and most of those on board. Helium, which has about 90 per cent of the buoyant effect of hydrogen, is preferable for such uses, but the lack of available supplies has limited its use.

The use of hydrogen in the oxyhydrogen blowpipe is mentioned in connection with the reactions of oxygen on page 42. A differ-ent type of high temperature burner, the atomic hydrogen blow-pipe, was developed by Langmuir about 1927. Hydrogen is com-posed of diatomic molecules, which decompose into single atoms with the absorption of a large amount of heat when the gas is blown through a very hot electric arc. The atoms reassociate rapidly in contact with metal surfaces, and heat equal to about 103,000 calories per mole is produced. Temperatures estimated to be between 4000° and 5000° may be obtained. Since the product of the combination of hydrogen atoms is gaseous hydrogen, an at-mosphere of this gas is retained continuously at the surface of the hot metal, and combination of the metal with oxygen is thus prevented.

Large quantities of hydrogen are now used in the production of synthetic ammonia and synthetic methanol. An important use of

hydrogen is in the hydrogenation of animal and vegetable oils to produce fats. In the process, hydrogen combines with unsaturated compounds in the oil to form saturated compounds having higher melting points. The hydrogenation of cottonseed oil is carried out at 200° in the presence of nickel as a catalyst, with hydrogen at a pressure of approximately 5 atmospheres. The products of the hydrogenation of such oils are used as edible fats, in soap making, and for many other purposes. Catalytic hydrogenation makes it possible to produce liquid fuels from coal and to increase the yield of gasoline during distillation and further treatment of petroleum.

WATER

The abundance of water in the liquid state in oceans, lakes, rivers, and as moisture in the soil, is a matter of common observation. Its occurrence as a gas in air, and as a solid in different places and seasons is also well-known. Animal and vegetable matter are largely composed of water; approximately 65 per cent of the human body and more than 90 per cent of green vegetables is water. Many dry rocks contain large proportions of water in combination with the other substances of which the minerals are composed.

Fig. 37. Electrolysis of Water

Composition of Water. An accurate determination of the composition of water was made by Morley, using a method in which he weighed directly the proportions of hydrogen, oxygen, and water. He obtained the average ratio of 1.0076 parts by weight of hydrogen to 8 parts by weight of oxygen. The volume ratio in which hydrogen reacts to produce water may be determined most simply by the electrolysis of water. The gases are collected separately by the use of an apparatus such as that shown in Fig. 37, in which the electrodes are sealed in opposite limbs of the tube. It is observed that the volume ratio is two of hydrogen to one of oxygen. The volume ratio of these gases to the water produced may be determined by employing temperatures and pressures at which water also is
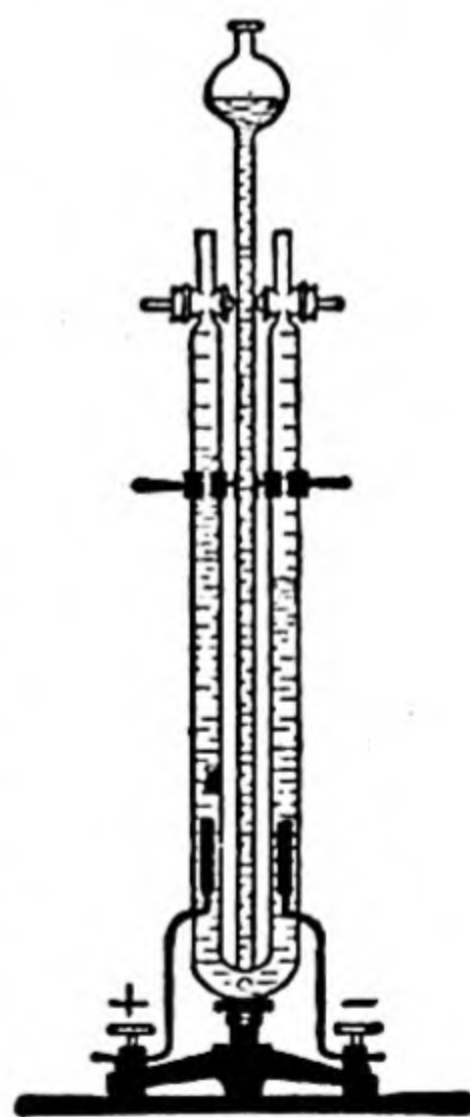
gaseous. In the apparatus shown in Fig. 38, hydrogen and oxygen — produced by the electrolysis of water in the volume ratio of two to one — are collected over mercury in a barometer tube. A constant temperature is maintained by passing steam through the outer jacket of the apparatus. The gases are ignited by a spark between the ends of wires sealed through the glass walls. The pressure is readjusted to the former condition by lowering the tube. It is now found that the volume of the gaseous water is two thirds that of the mixed gases or equal to the volume of hydrogen and double the volume of oxygen involved in the reaction. Applying Avogadro's hypothesis, it is evident that the number of molecules of water produced in this reaction is equal to the number of molecules of hydrogen and double the number of molecules of oxygen entering into the reaction.
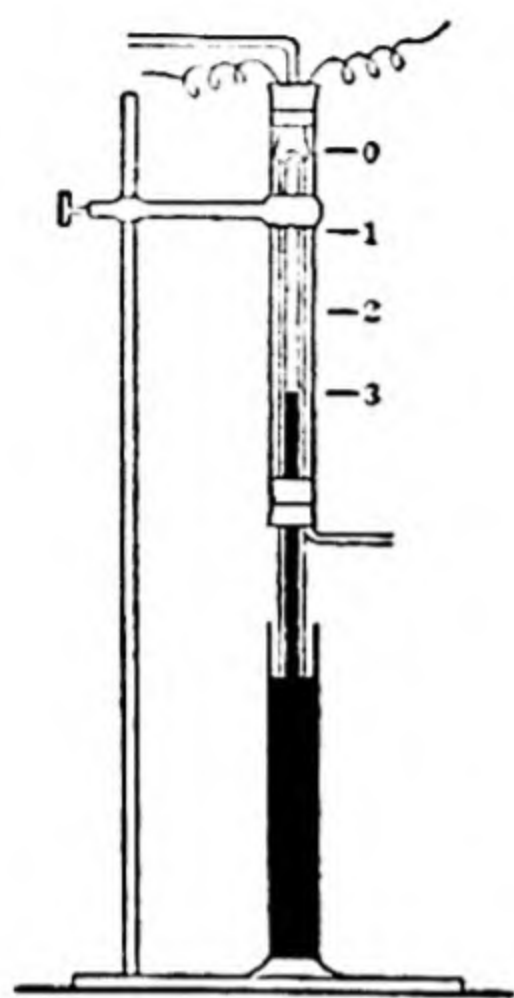
Fig. 38. Combination of Hydrogen and Oxygen

Properties of Water. Liquid water in thin layers appears to be colorless, but in deep layers it has a bluish-green color. Pure water is odorless and tasteless. Natural waters usually have taste because of the presence of dissolved substances. Water is a poor conductor of electric current.

Several common units of measurement are defined in terms of the properties of water. The melting point of ice and the boiling point of water at a pressure of one atmosphere have been selected arbitrarily to establish the fixed points, 0° and 100°, respectively, on the centigrade scale of temperature. *One degree* is, therefore, the one hundredth part of the temperature range between the normal freezing and boiling points of water. *One calorie* is the amount of heat required to raise the temperature of one gram of water one degree from 14.5° to 15.5°. *The specific heat* of a substance is the ratio of its heat capacity to that of water. Water has a higher heat capacity than most of the common substances of which rocks and soil are composed. Therefore, large bodies of water exert a moderating influence on atmospheric temperatures in the vicinity.

The density of a substance is the weight of unit volume at the prescribed temperature. One milliliter of water weighs one gram

at 4°. *The specific gravity* of a solid or liquid is equal to the ratio of its density to the density of water at 4° or other specified temperature. The heat of fusion of water is 80 calories per gram. The extensive use of ice as a refrigerant is, of course, based on this property. The density of ice is lower than that of the liquid, so that ice forms on the surface of a body of water. If the contraction in the volume continued during the cooling and solidification of water, as it does for many substances, ice would sink to the bottom and bodies of water would freeze completely during prolonged cold weather. The heat of vaporization of water is 540 calories per gram. Consequently, steam possesses a great deal more energy than liquid water at the same temperature. The volume of steam is approximately 1700 times that of liquid water at the boiling point.

Deuterium Oxide. Heavy Water. The properties of the oxide of deuterium are similar to those of water but there are small differences. Deuterium oxide is present in ordinary water in small proportions, approximately 1 molecule in 5000. Ordinary water decomposes more rapidly than deuterium oxide during electrolysis, thus increasing the concentration of the heavy water. G. N. Lewis produced pure deuterium oxide by preparing deuterium and combining it with oxygen. The density of deuterium oxide is 1.1079 g. per ml. at 25°; the freezing point, 3.8°; the temperature of maximum density, 11.6°; the boiling point, 101.4°; and the heat of vaporization approximately 260 calories per mole greater than for ordinary water.

Reactions of Water. Relatively large amounts of heat are evolved in the union of hydrogen and oxygen, and water is stable toward heat. It is decomposed into the elementary gases to the extent of only 1.8 per cent at 2000°. The decomposition reaction is reversible, and a state of equilibrium is established in a closed system.

$$2\,H_2O \rightleftharpoons 2\,H_2 + O_2 - 113{,}120 \text{ cal.}$$
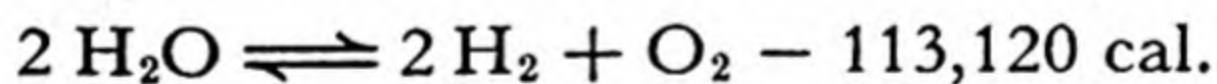
The reaction of active metals with water, forming hydrogen and the hydroxide of the metal, is discussed in a preceding paragraph.

$$2\,Na + 2\,H_2O \longrightarrow H_2 + 2\,NaOH$$
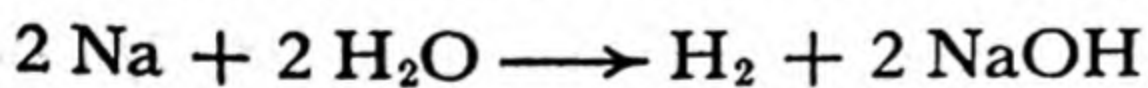
Its reactions with some of the metal oxides and nonmetal oxides are discussed in Chapter IV.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$P_2O_5 + 3 H_2O \longrightarrow 2 H_3PO_4$$
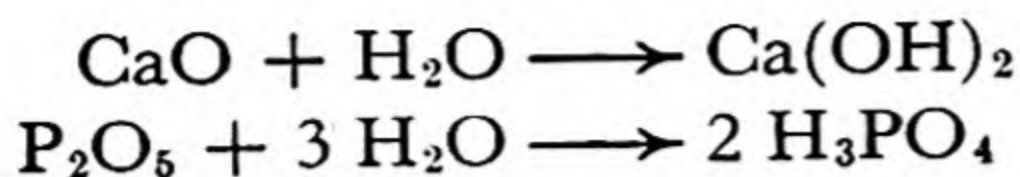
A number of binary compounds of two nonmetals with each other are decomposed by water. Thus, phosphorus trichloride reacts with water to form hydrochloric acid and phosphorous acid.

$$PCl_3 + 3 H_2O \longrightarrow 3 HCl + H_3PO_3$$
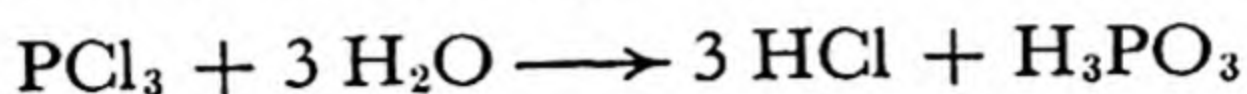
Some binary compounds containing metals are also decomposed by water. The hydride of calcium reacts with water to form calcium hydroxide and hydrogen.

$$CaH_2 + 2 H_2O \longrightarrow Ca(OH)_2 + 2 H_2$$
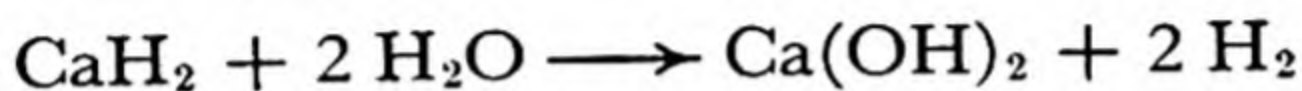
Calcium carbide reacts with water forming calcium hydroxide and acetylene.

$$CaC_2 + 2 H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
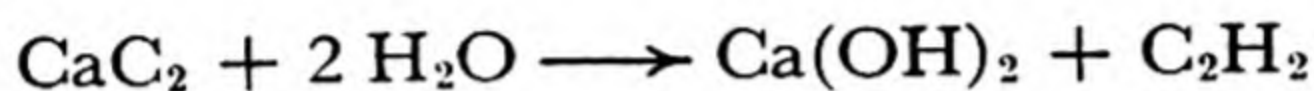
This type of reaction is called *hydrolysis, a double decomposition in which water is one of the reactants.* A number of salts react more or less extensively with water, but the hydrolysis of salts involves principles not yet introduced. Consequently, the further discussion of this reaction is deferred to Chapter 17.

Hydrated Compounds. Many compounds combine with water to form products known as hydrates. When a solution, prepared by dissolving anhydrous cupric sulfate in water, is allowed to evaporate, a mass of irregular blue crystals is obtained. When these crystals are dried — to remove the water held mechanically — and are then heated, water is driven out, leaving a white residue of anhydrous copper sulfate. The blue crystalline material contains copper sulfate and water in the molar ratio of one of copper sulfate to five of water, $CuSO_4(H_2O)_5$.

Hydrated compounds differ in stability. Stable ones do not readily release water at ordinary temperatures, and the pressure of water vapor in the air, required to prevent decomposition, is low. Unstable hydrates give up water so readily that a relatively high pressure of water vapor is required to prevent decomposition. The hexahydrate of strontium chloride, $SrCl_2(H_2O)_6$, decomposes to form the dihydrate according to the equation:

$$SrCl_2(H_2O)_6 \rightleftharpoons SrCl_2(H_2O)_2 + 4 H_2O$$
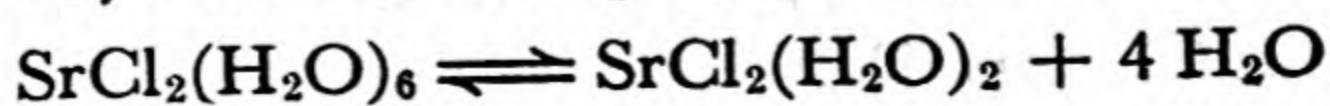
The pressure of water vapor required to maintain this equilibrium at 20° is 5.65 mm. The hydrate spontaneously decomposes if it is exposed to air at 20° with a relative humidity of 30, because the pressure of the water vapor in the air under these conditions is only 5.25 mm., 30 per cent of 17.5 mm. If, however, the relative humidity is 40 and the temperature 20°, the pressure of water vapor is 7 mm., and this hydrate does not decompose. The spontaneous decomposition of a hydrate, with the formation of either a lower hydrate or the anhydrous substance, is called *efflorescence*. Salts which yield hydrates requiring low pressures of water vapor to maintain equilibrium may be used to dry gases.

Solvent Action of Water. A greater number of common substances dissolve in water than in any other liquid. The amount of different substances which can be dissolved by the same quantity of water varies, depending on the specific properties of the substance. In some solutions the relative quantity of the dissolved substance is large and in others small. The general properties of solutions are discussed in the following chapter.

Natural Waters. Rain water, formed by the condensation of water vapor in the air, is nearly pure water, containing only small proportions of dust and of dissolved gases. As water flows over the surface of the earth and seeps down through the soil, soluble substances are leached out, and finely divided solids may be carried along in suspension. Consequently, water in streams and lakes contains impurities held partly in solution and partly in suspension. The suspended materials may be of mineral origin, as sand and clay, or of organic origin, as living microorganisms or dead animal or vegetable matter. The dissolved materials may be soluble solids, liquids, or gases.

Most of the suspended solids settle out when the velocity of the running water decreases, forming sand or mud banks. Very finely divided particles may fail to settle. Dissolved solids do not settle, nor do they evaporate with water. Consequently, the concentration of mineral matter in sea water slowly increases. Sea water contains approximately 3.6 per cent of mineral matter in solution.

Water Supplies. As the density of population increases and industrial developments become more extensive, the problem of securing an adequate supply of water becomes greater. The suita-

bility of water for different specific uses depends on the nature of the impurities it contains. Water used in steam boilers should be free from substances that cause corrosion and scale formation. Water for laundry should not contain substances that react with soap and thus cause waste. Potable water should be free from all materials hazardous to health and from substances with disagreeable odor or taste. Except in rural sections, the water from uncontaminated springs and wells is no longer sufficient to meet the demand. Only in sparsely settled regions can one be sure that it is safe to drink from surface streams. Reservoirs are constructed in suitable water courses; and, in many instances, a city water supply must be brought through aqueducts for many miles. Large areas of land surrounding such reservoirs are closed to trespass in order to avoid contamination of the water.

Water Treatment. The treatment of water, making it suitable for use, depends on the impurities it contains and on the uses for which it is intended. Suspended matter is removed by settling and by filtration, but dissolved substances require chemical treatment. Dissolved salts of calcium and magnesium are particularly objectionable in water intended for use in steam boilers and in laundries. Such water is known as hard water. The treatment of water to remove such substances is considered later, along with calcium and magnesium compounds.

In general, disease germs are the most dangerous impurities in potable water. The minute organisms may be attached to larger particles of suspended matter, but clear water may also contain such microorganisms. Many epidemics of disease have been traced to the contamination of water by sewage, e.g., typhoid fever and cholera. Since it is usually impossible to prevent the entrance of sewage into streams from which city water is secured, the water must be treated to ensure its safety. The treatment usually involves clarification of the water, followed by the use of disinfectants. The customary method of clarifying water consists in filtering it through beds of sand. Substances such as alum and lime or ferrous sulfate and lime are added to produce gelatinous precipitates, which aid in the coagulation and removal of suspended matter. The clear water is then disinfected usually by the action of chlorine in controlled proportions.

Pure water is required for many uses in the chemical industry. It is usually obtained by the distillation of water after removal of suspended matter. Steam from the boiling water passes out of the distilling flask into the condenser. The liquid product is collected in a clean receiver. Impurities that are not volatile at the temperature of boiling water remain in the distilling flask. Water may be chemically treated before distillation to remove certain volatile compounds and organic matter. Water attacks glass slowly and dissolves materials from it when stored in glass vessels. Tin condenser tubes and receivers are used frequently for distilled water, since tin is not appreciably attacked by water.

EXERCISES

1. Write equations to represent several reactions yielding hydrogen as a product.
2. What is meant by a reversible reaction? a state of equilibrium? How is the completion of a reversible reaction caused?
3. Describe the industrial production of hydrogen by the reaction of steam with coke.
4. Discuss important uses of hydrogen, indicating in each instance the properties which suit it for the particular application.
5. Describe experiments determining the molecular ratio in which hydrogen and oxygen react to produce water.
6. Name and define units of measurement based on properties of water.
7. Write equations to represent reactions of water.
8. What is a hydrate? What conditions determine whether a hydrate will effloresce or an anhydrous material will become hydrated?
9. What are the sources of impurities in natural water in rivers, lakes, and oceans?
10. What steps are required to secure a suitable supply of water for domestic use?

SUPPLEMENTARY READINGS

Weeks, M. E., *The Discovery of the Elements*, Journal of Chemical Education, Easton, Pa., 1935, pp. 29–33.

Taylor, H. S., *Industrial Hydrogen*, Reinhold Publishing Corporation, New York, 1925.

Jaffe, B., *Crucibles*, Simon and Schuster, Inc., New York, 1930, sec. V.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chap. 13.

Furnas, C. C., *Rogers Manual of Industrial Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, chap. 6.

Chapter 7

SOLUTIONS

The dissolving of different substances in liquids is a familiar process. The particles of the dissolved solids are so small as to be invisible. They do not settle, and cannot be separated from the liquid by filtration. These particles become dispersed so uniformly throughout the liquid that the composition of a solution is the same in all portions. Nevertheless, the proportions of the materials in a solution may be varied. *A solution is a homogeneous mixture of two or more materials.* The particles of the dissolved substances are molecules in some solutions and in others, electrically charged particles called ions. Many of the chemical reactions take place in solution, frequently in aqueous solution, and involve the interaction of these unit particles.

Types of Solutions. The dissolved substance in a solution is called the solute and the dispersing medium the solvent. Substances in each of the three states of matter may be solutes, and may serve also as solvents. Solutions may be grouped for study into three different types according to the final phase under the experimental conditions. Solid solutions are composed of mixed crystals. Liquid solutions may be formed by dissolving solids, liquids, or gases in liquids. They are the most familiar of the three classes of solutions. If both of the materials in the solution are liquids, either might be called the solute or the solvent. Commonly, the more familiar liquid, or the one present in the larger proportion, is called the solvent.

The Solution of a Solid in Water. The dissolving of one substance by another depends on the properties of each. When a soluble solid, such as cane sugar, is placed in a beaker of water, it becomes dispersed into molecules which move about freely in the liquid as dissolved particles. The process is the dissolving of the solid. Some of the dissolved particles approach the surface of

the solid and are attracted back into an appropriate position in the crystal. This process is the crystallization of the solute. The rate of crystallization increases as the concentration of the solute in the solution becomes greater. When an excess of the solid has been added to the liquid, the rates of these two changes become equal. The solution is now saturated, and no further change in concentration takes place unless the conditions are altered. *A saturated solution contains the concentration of the solute required for equilibrium with the undissolved material at the specified temperature and pressure.*

Solubility. The relative amount of a solute in its saturated solution at each temperature is constant. *The solubility of a substance is the amount required to saturate a specified quantity of the solvent.* These quantities may be expressed in different units. The solubility of solids and liquids in a liquid is usually stated as the number of grams required to saturate 100 g. of the solvent. The solubility of a gas is usually stated as a volume ratio. Substances of very low solubility, such as barium sulfate, 0.00023 g. in 100 g. of water, are frequently called insoluble. These substances are not truly insoluble, but they are so slightly soluble that the concentration of the saturated solution is too small to be significant.

Conditions Affecting the Solubility of Solids in Liquids. The solubility of a substance in a particular solvent is a specific property. A substance is generally more soluble in a solvent composed of similar particles than in one with dissimilar particles. There is no single theory that can account fully for the solubility and insolubility of substances.

The solubility of a solid in water varies to some extent, depending on the *size of the crystals.* Very small crystals dissolve more rapidly than larger crystals of the same substance. Hence, in the presence of both large and small crystals, the concentration maintained by the finely divided material is greater than that required for equilibrium with the coarser particles. Therefore, the small crystals dissolve and the larger ones increase in size when such a suspension is allowed to stand. The greater solubility of the finely divided material is attributed to the greater surface area for the same weight of material.

The effect of changes of temperature on solubility is best understood by a consideration of the energy changes that accompany the solution

of the substance. Whenever a change in state occurs, changes in energy take place, but energy changes may not be involved if both substances are in the same state, as in the mixing of gases. The dissolving of a solid by a liquid is an endothermic change. If a change in the state of the solute alone were involved, the same amount of heat would be absorbed as is required to melt an equal weight of the substance. Dissolving a solid hydrocarbon in a liquid hydrocarbon of the same chemical nature approximates this condition. Usually the changes are much more complex than this, and the heat necessary to melt the solid is only a portion of the energy change. There is no regularity in the effect of temperature on the solubility of solids. The solubility of potassium nitrate is 13 g. in 100 g. of water at 0°, but increases to 246 g. at 100°. The solubility of sodium chloride increases from 35.6 g. in 100 g. of water at 0° to only 39.8 g. at 100°. The solubility of some solids decreases with rise in temperature.
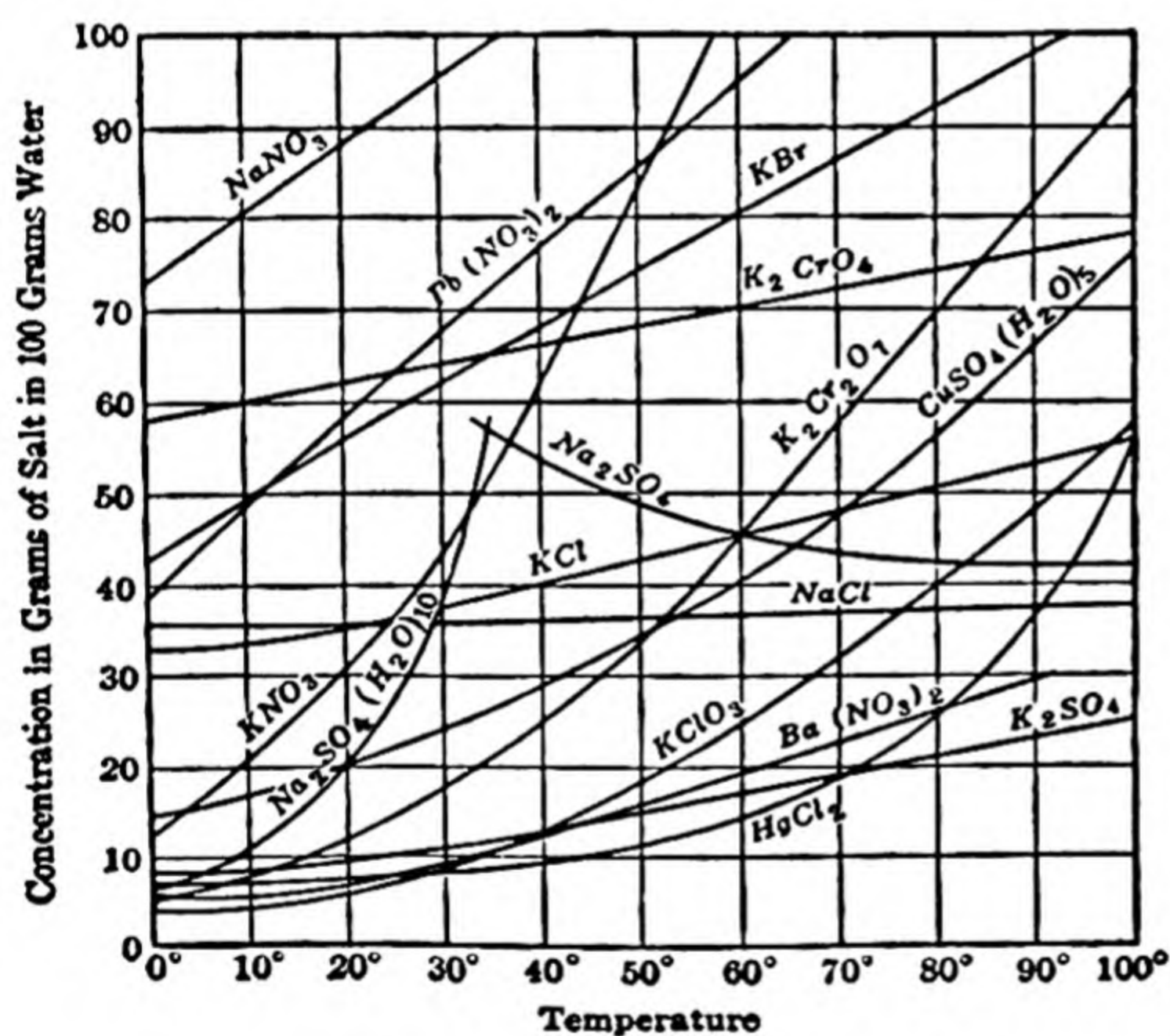
Fig. 39. Solubility Curves

Thus, the solubility of calcium sulfate is 0.759 g. in 100 g. of water at 0° and only 0.162 g. at 100°.

Solubility Curves. Solubility data are represented in a convenient manner by means of solubility curves. The solubilities of the solute, expressed in grams in 100 g. of the solvent, are usually represented along the vertical axis and the temperatures on the horizontal axis. A smooth curve may be drawn for each substance, connecting the points that represent experimental determinations of solubility. (Fig. 39.) The curve describes the solubility over the entire range of temperature. A break in a solubility curve, as

shown for sodium sulfate, indicates a transition point where the composition of the solid phase in equilibrium with the saturated solution undergoes change. Below the transition temperature of this solute, 32.4°, the solid phase involved in the equilibrium is sodium sulfate decahydrate, $Na_2SO_4(H_2O)_{10}$. At higher temperatures, the solid phase is the anhydrous salt. Both solids may exist in equilibrium with the same solution at the transition temperature.

Supersaturated Solutions. The hot saturated solution of a salt usually contains a greater concentration than the cold solution, because the solubility of salts usually increases with rise in temperature. In many instances, the hot concentrated solution may be cooled without crystallization of the solute. The saturated solution in equilibrium with hydrated sodium sulfate crystals at 30° contains 40 g. in 100 g. of water, measured as the anhydrous salt to which it is equivalent. This solution may be cooled to 15° without change in composition if it is filtered while still hot, so as to remove the excess of the solid. The solubility of sodium sulfate at the lower temperature is 13 g. in 100 g. of water. Nevertheless, the quantity that dissolved at the higher temperature remains in solution under these conditions. Solutions such as this contain a greater concentration of the solute than the equilibrium quantity. Such solutions are known as *supersaturated solutions*. If a minute fragment of the solid phase is added to the supersaturated solution, the excess of the solute rapidly crystallizes. The addition of a crystal of the solute to induce crystallization from a supersaturated solution is known as "seeding the solution."

Solutions of Gases in Liquids. Solutions of soluble gases are usually prepared by bubbling the gas through the liquid, or by enclosing it over the liquid. As the concentration of the gaseous substance in the solution increases, the rate at which it returns to gaseous state also increases. When these two changes — the solution of the gas and its evaporation — take place at the same rate, the solution is saturated. Dissolving a gas in a liquid is an exothermic change, because it involves converting gas into a liquid. Consequently, the solubility of a gas decreases with increasing temperature.

The solubility of a gaseous substance at fixed temperature increases directly with the pressure. The rate at which a specific gas

dissolves increases directly with the concentration in the gas phase. Hence, the concentration in the solution must increase in the same ratio to maintain equilibrium. If the pressure of a gas in contact with a solution at constant temperature is doubled, the molecular concentration in the gas phase is doubled, causing the solubility of the substance by weight to become twice as great. This relationship is stated as **Henry's Law: At constant temperature, the solubility by weight of a gas is directly proportional to the pressure.** This law applies only to gases which are not highly soluble and which do not react with the solvent.

The partial pressure of each gas in a mixture is proportional to its molecular concentration. Since the solubility of a given gas is also proportional to its molecular concentration, the solubility of a gas from a mixture is proportional to its partial pressure. The solubility of oxygen from a gas mixture containing 20 per cent of oxygen molecules at 760 mm. is the same as the solubility of pure oxygen at a pressure of 152 mm. A soluble gas may be removed rapidly from a solution by passing air through the boiling solution. Bubbles of gases of low solubility sweep away the escaping gas and reduce its partial pressure virtually to zero.

Solutions of Liquids in Liquids. Liquid Pairs. Some pairs of liquids, like alcohol and water, dissolve in each other in any proportion. Such liquids are completely miscible. Others dissolve to a limited extent and are called partially miscible, *e.g.*, ether and water. If a quantity of ether, too great to be dissolved completely, is shaken with water and the mixture is allowed to stand, separation into two layers occurs. The upper layer is a saturated solution of water in ether, and the lower layer of ether in water. The concentrations in each layer are definite at a fixed temperature, regardless of the relative amounts of the two substances. In general, the solubilities of two partially miscible liquids in each other increase with the temperature. Liquids which are not appreciably soluble in each other are called immiscible liquids.

Extraction. Some solutes are soluble in each of two immiscible or partially miscible liquids, but are more soluble in one liquid than in the other. Iodine, for example, is about 200 times more soluble in ether than in water. If a solution of iodine in water is shaken with an equal volume of ether and then allowed to stand,

the mixture separates into two layers. Iodine is found to be present in each layer, and a condition of equilibrium between the iodine dissolved in the two layers is established. (Fig. 40.) The concentration of iodine in the ether layer is approximately 200 times that in the water layer. This is a particular instance covered by the **Law of Partition: A solute, which is soluble in each of two immiscible or partially miscible liquids, becomes distributed between the two in such quantities that its concentrations in the two solutions are in the same ratio as its solubilities in the two solvents.** Removing a solute more or less completely from one solution or material by a liquid in which it is more soluble is a process called *extraction*. The process has many important applications in the separation and purification of industrial products.

Fig. 40. Extraction

The Concentration of Solutions. The concentration of a single substance is defined by weight in unit volume. The quantity of both solute and solvent is required to express the concentration of a solution. A dilute solution contains only a relatively small proportion of the solute, and a concentrated solution contains a relatively large proportion. These terms have no quantitative significance except such as may be assigned arbitrarily. The proportions of the substances in a complex material are ordinarily stated as *weight per cents*. Thus, a 10 per cent solution of a salt in water contains 10 g. of the salt in 90 g. of water, producing 100 g. of solution. No significant relationship in the properties of solutions can be derived from the weight percentages of different solutes.

Solutions are extensively used to supply a solute for chemical reactions. For such uses, it is customary to express the quantity of the solute in chemical units of weight in one liter of solution. One of the familiar chemical units is the mole. Using the mole as the weight unit of the solute, the concentration of the solution is expressed as the molarity. *The molarity of a solution is equal to the number of moles of the solute in one liter of solution*, the volumes generally being measured at 20°. The ratio by volume in which solutions of the same molarity react is necessarily the same as the molar ratio. The volume of one molar, 1 M., sulfuric acid required to neutralize

500 ml. of a one molar solution of sodium hydroxide is easily calculated. The molar ratio in which these substances react is shown by the equation:

$$2 \, NaOH + H_2SO_4 \longrightarrow 2 \, H_2O + Na_2SO_4$$
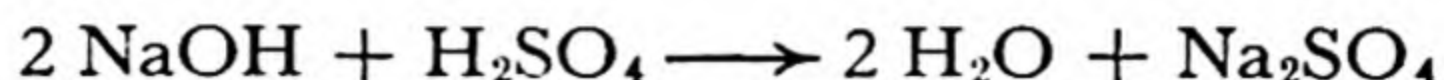
Only one half as many moles of sulfuric acid are required as of sodium hydroxide. Since equal volumes of solutions of the same molarity contain the same number of moles, the volume of the sulfuric acid required for this reaction is one half the volume of sodium hydroxide, *i.e.*, 250 ml.

The equivalent weight may be used as the unit quantity of the solute. The concentration of the solution is then expressed as normality. *The normality of a solution is equal to the number of gram equivalent weights of the solute in one liter of solution.* The gram equivalent weight of a compound is the weight that contains one gram equivalent of an element or radical. The gram equivalent weight is the weight corresponding to a valence of 1, or to unit change in valence, for each of the atoms of a particular variety involved in the reaction. The gram equivalent weight of sulfuric acid in its general acid reactions is based on hydrogen, not oxygen, because the oxygen atoms in this compound are constituent parts of a complex radical. The gram equivalent weight of this compound is, therefore, the weight which contains one gram equivalent of hydrogen, 1.008 g. One mole, 98.076 g., of sulfuric acid contains 2.016 g. of hydrogen. Hence, the gram equivalent weight of sulfuric acid is 49.038 g. The weights of several solutes in one liter of solutions of the same normality and molarity are shown in Table 5.

TABLE 5. WEIGHTS OF THE SOLUTE (IN GRAMS) FOR SOLUTIONS OF DIFFERENT CONCENTRATIONS

Substance	1 M.	0.5 M.	1 N.	0.5 N.
Hydrochloric acid, HCl	36.45	18.22	36.45	18.22
Phosphoric acid, H_3PO_4	98.00	49.00	32.66	16.33
Calcium chloride, $CaCl_2$	111.00	55.50	55.50	27.75
Cupric nitrate, $Cu(NO_3)_2$	187.60	93.80	93.80	46.90
Aluminum sulfate, $Al_2(SO_4)_3$	342.00	171.00	57.00	28.50
Ammonium sulfate, $(NH_4)_2SO_4$	132.00	66.00	66.00	33.00
Calcium hydroxide, $Ca(OH)_2$	74.00	37.00	37.00	18.50

Equal volumes of solutions of the same normality are equivalent to each other. If the solutions are not of the same normality, the

volumes required for reaction are inversely proportional to the normalities. The volume of a solution of specified normality required to react with a given weight of a substance may be calculated by the method illustrated in Chapter 2, page 30, except that the molar ratio is expressed in terms of the volume of this solution. Suppose that the problem is to calculate the volume of 0.5 N. hydrochloric acid required to react with 10 g. of calcium carbonate.

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

One mole of calcium carbonate is 100 g. and 4 liters of 0.5 N. hydrochloric acid are required to furnish 2 moles.

$$\frac{X \text{ liters of HCl}}{4 \text{ liters of HCl}} = \frac{10 \text{ g. of CaCO}_3}{100 \text{ g. of CaCO}_3}$$
$$X = 0.1 \times 4 = 0.4 \text{ liter of 0.5 N. HCl}$$

Some of the properties of solutions are dependent on the relative numbers of solute and solvent particles. Solutions of the same molarity and of the same normality may differ greatly in the relative numbers of solute and solvent particles they contain, because of the volume changes that occur when the solute is dissolved. In the investigation and application of these effects it is convenient to employ still a different system for the designation of concentration. This system is based on the use of a specified weight of solvent instead of a specified volume. The same weight of a given solvent always contains the same number of molecules. The concentration on this basis is expressed as the molality. *The molality of a solution is equal to the number of moles of the solute dissolved in 1000 g. of the solvent.* If the solute becomes dispersed into other particles than molecules, or reacts with the solvent, it is clear that the relative numbers of free solute and solvent particles will differ from molecular dispersions of the same molality.

The mole fraction is a significant ratio for a number of important scientific relationships. *The mole fraction is the ratio of the number of moles of one compound to the total number of moles in the solution.* In a solution containing one mole of ethyl alcohol in nine moles of water, the mole fraction of the alcohol is 1 mole in 10, or 0.1, and the mole fraction of water is 0.9. *Mole per cent* is this same ratio based on 100 moles of the mixture. The solution just considered

contains 10 mole per cent of ethyl alcohol and 90 mole per cent of water.

Since the composition of solutions is not definite, obviously, the concentration of the solute may be varied as is convenient for the purpose to which the solution is applied. A number of units expressing the concentration of solutions have been defined in this section. For some purposes one unit is preferable, while for other considerations another is better. Therefore, one should select the system best suited for the particular problem.

PROPERTIES OF SOLUTIONS

Many physical properties of solutions differ from those of both the solute and the solvent. Solutions of solids and gases in liquids are liquid solutions, but a characteristic color, odor, or taste may be imparted by the presence of the solute. The density of the solution of a solid in a liquid is usually greater than the density of the solvent. Consequently, a saturated solution is formed about the solute when a quantity of a solid is placed in a beaker of water, and the solid dissolves slowly because the dissolved material diffuses very slowly into the upper, less dense, unsaturated solution. Shaking or stirring increases the rate of solution by maintaining a more nearly uniform concentration throughout. The solute affects the vapor pressure and, consequently, the boiling point and the freezing point of the solvent. Solutions of nonvolatile solutes are treated before the solutions of liquids in liquids with both the solute and the solvent volatile.

Lowering of the Vapor Pressure of the Solvent. The vapor pressure of a liquid is decreased by the addition of a nonvolatile solute. This is due to a decreased rate of evaporation, and a lower concentration of the vapor is sufficient for equilibrium. The solute becomes uniformly distributed throughout the solution, and thus decreases the molecular concentration of the solvent. It is found by experiment that equal weights of different solutes, such as dextrose, glycerol, and glycol, dissolved in the same weight of water have different effects on the vapor pressure. An equal number of moles of each of these solutes, however, in the same weight of water causes the same effect. Hence, the effect is believed to be due to the relative numbers of molecules, not to the variety. This

conclusion may be stated as **Raoult's Law: The vapor pressure of a liquid solvent is proportional to its mole fraction in the solution. The lowering of the vapor pressure of the solvent is proportional to the mole fraction of the solute.** These relationships are shown by the following equations in which p is the vapor pressure of the solvent in equilibrium with the solution, and p^0 is the vapor pressure of the pure solvent; N_1 is the mole fraction of the solvent and N_2, the mole fraction of the solute:

$$p = p^0 N_1$$
$$p^0 - p = p^0 N_2$$

In its fundamental form this law applies rigidly only to ideal solutions. *An ideal solution* is one in which no change in energy accompanies the mixing of materials in the same state, and, if the solute and solvent are in different states, the energy change is equivalent to that accompanying the change in phase. In such solutions the solute would be in the form of single molecules, which have no effect on each other or on molecules of the solvent other than the diluting effect due to their presence. Most solutions are not ideal, but Raoult's law is applicable as an approximation of the vapor pressure effects caused by many solutes. Deviations from Raoult's law may be attributed to forces of attraction of solute particles for each other, thus diminishing their effect on the solvent. These forces are decreased by dilution, because the average distances between the particles are greater in the more dilute solutions. Solutions so dilute that the deviations from Raoult's law are no longer significant are called *infinitely dilute solutions*.

The simple form of Raoult's law may be applied in solutions of ordinary concentration through the introduction of an empirical constant. This constant, known as the *activity coefficient*, takes into account deviations from ideality caused by forces existing in solution. In terms of activity coefficients, the equations for the two forms of the vapor pressure law are:

$$p = p^0 (f_1 N_1)$$
$$p^0 - p = p^0 (f_2 N_2)$$

The functions represented by f_1 and f_2 are evaluated from experimental data describing the behavior of substances in solution.

The quantity obtained as the product of the mole fraction and activity coefficient is known as the *activity*, a function introduced by G. N. Lewis.

The deviations are greater in concentrated than dilute solutions. The vapor pressure effects caused by acids, basic hydroxides, and salts in aqueous solution are much greater than those summarized by Raoult's law.

An approximate form of Raoult's law of vapor pressure depression may be stated in terms of molal concentrations. The number of moles of the solute in dilute solutions is small compared to the number of moles of the solvent. Consequently, the difference between the mole fraction and the molar ratio of solute and solvent is so small that the two may be considered as approximately the same. In a solution containing 0.1 mole of solute in 1000 g. of water, the number of moles of water is 55.55, and the total number of moles, 55.65. The mole fraction of the solute in this solution is 0.1/55.65 or 0.00179. In 0.2 molal solution, the mole fraction is 0.2/55.75 or 0.00358. Since the vapor pressure depressions in the two solutions are proportional to the mole fractions of the solute, they are in the ratio of 0.00179 to 0.00358, or one to two. But, these numbers are in the same ratio as the molalities of the two solutions. Hence, the lowering of the vapor pressure of the solvent is approximately proportional to the molal concentration of the solute.

Deliquescence. Drying Agents. The pressure of water vapor in equilibrium with concentrated solutions is less than the pressure of water vapor normally in air. Such solutions absorb moisture from the air. This may be illustrated by placing a beaker containing a concentrated solution of calcium chloride and a beaker of water under a bell jar. (Fig. 41.) Pure water has a higher vapor pressure than the calcium chloride solution. Hence, water continually evaporates and condenses in the calcium chloride solution until all of the water has distilled into the solution. Highly soluble solids exhibit the property of absorbing moisture from the air. At first, a small volume of saturated solution is formed at the sur-
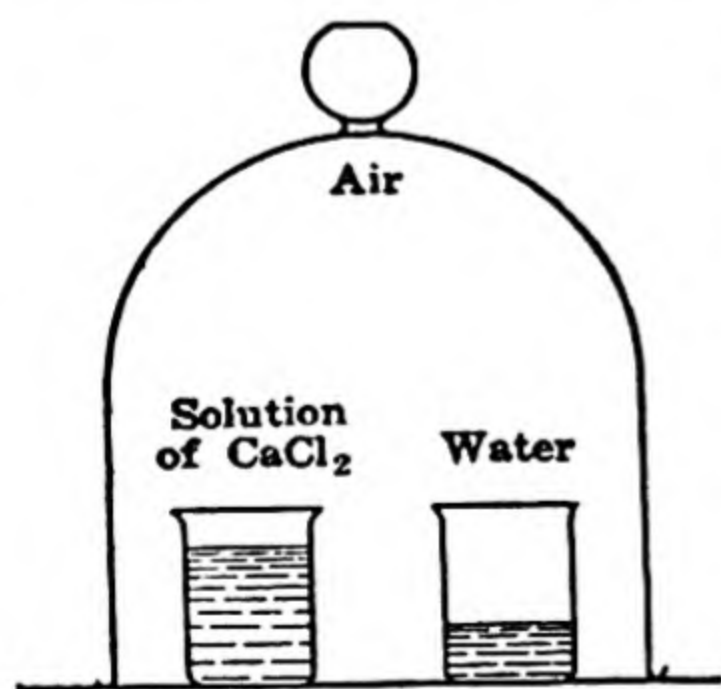
Fig. 41. Deliquescence

face of the solid, and water condenses into this solution as described. The solution becomes more dilute when exposed to air, and the pressure of water vapor, required for equilibrium, increases with the dilution until it becomes equal to the pressure of water vapor in the air. The absorption of water from the air with the formation of a solution is called *deliquescence*. Because of this property, calcium chloride is used on dirt roads to absorb moisture and prevent dust.

There are a number of substances that absorb moisture. Some of these substances are suitable for use as drying agents. Substances so highly soluble that their solutions have very low vapor pressures are good drying agents. The dehydrating action of sodium hydroxide, potassium hydroxide, and, in part, of calcium chloride and sulfuric acid, may be ascribed to this property. Some drying agents combine with water to form hydrated compounds that may stand in equilibrium with only small pressures of water vapor. Anhydrous copper sulfate, calcium sulfate, calcium chloride, and sulfuric acid are drying agents of this type. Concentrated sulfuric acid is often used in a desiccator (Fig. 42) to provide a dry atmosphere. The exposed surface may be greatly increased by pouring the acid over an inert substance. The chemical reaction of some of the oxides with water reduces the pressure of water vapor to very low

Fig. 42. Desiccator

values. Such oxides are good drying agents. Phosphorus pentoxide reacts with water to form phosphoric acid, and the oxides of barium and calcium yield hydroxides. Another group of substances with very porous structure absorb water in the many fine capillaries.

Elevation of the Boiling Point of the Solvent. The normal boiling point of a liquid is the temperature at which its vapor pressure is equal to 760 mm. Since the presence of a nonvolatile solute lowers the vapor pressure of the solvent, it is obvious that the vapor pressure of a solution is less than 760 mm. at the normal boiling temperature of the pure solvent. Therefore, it is necessary to heat an aqueous solution of a nonvolatile solute to a temperature above 100° to raise the vapor pressure to 760 mm. (Fig. 43.) According to Raoult's law, the lowering of the vapor pressure of the

solvent depends on the mole fraction of the solute. Consequently, *the elevation of the boiling point of the solvent is directly proportional to the*
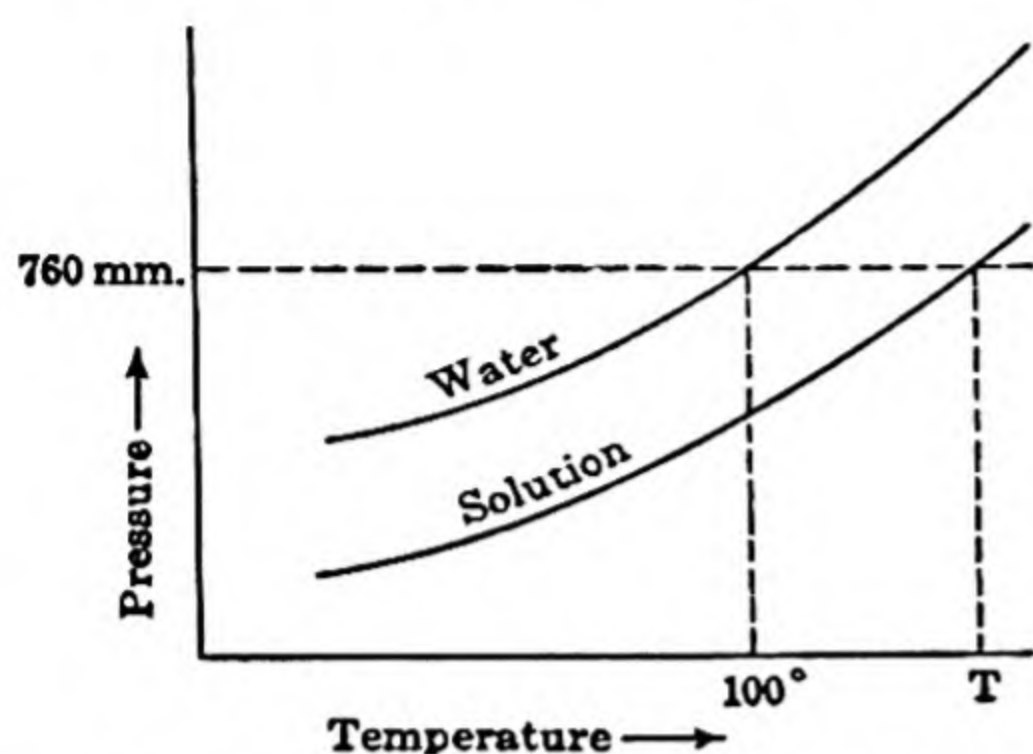
Fig. 43. Boiling Point Elevation

mole fraction of the solute, approximately proportional to the molality of the solution. Acids, basic hydroxides, and salts cause an elevation of the boiling point of water greater than proportional to the molality of the solution. The elevation of the boiling point of a solvent in a one molal solution is known as *the molal elevation of the boiling point.* The molal elevation of the boiling point is shown for several liquids in Table 6.

TABLE 6. MOLAL ELEVATION OF THE BOILING POINT OF SEVERAL SOLVENTS

Solvent	Boiling Point (° C.)	Molal Elevation (° C.)
Water	100.0	0.52
Benzene	80.3	2.43
Acetic acid	118.1	2.93
Ethanol	78.5	1.14
Chloroform	61.2	3.41
Naphthalene	218.0	5.80
Ethyl ether	34.5	2.01
Phenol	183.0	3.00

Depression of the Freezing Point of the Solvent. A lower temperature is required to freeze salt water than fresh water. The use of alcohol or other solutes in the water in automobile radiators is a familiar application of freezing point depression. The effects of various weights of several substances in the same weight of water are shown in Table 7.

TABLE 7. DEPRESSION OF THE FREEZING POINT OF WATER IN DEGREES CENTIGRADE
(1000 g. of water in each solution)

Compound	Formula	Molecular Weight	CENTIGRADES PER			
			10 g.	20 g.	30 g.	0.1 Mole
Dextrose	$C_6H_{12}O_6$	180	0.10	0.20	0.30	0.186
Ethanol	C_2H_5OH	46	0.40	0.80	1.20	0.186
Methanol	CH_3OH	32	0.58	1.16	1.74	0.186
Glycerol	$C_3H_8O_3$	92	0.20	0.40	0.60	0.186
Glycol	$C_2H_6O_2$	62	0.30	0.60	0.90	0.186

The freezing point depression caused by equal weights of glycol, glycerol, and dextrose in the same weight of water are shown by the curves in Fig. 44. These effects differ greatly, but the effects
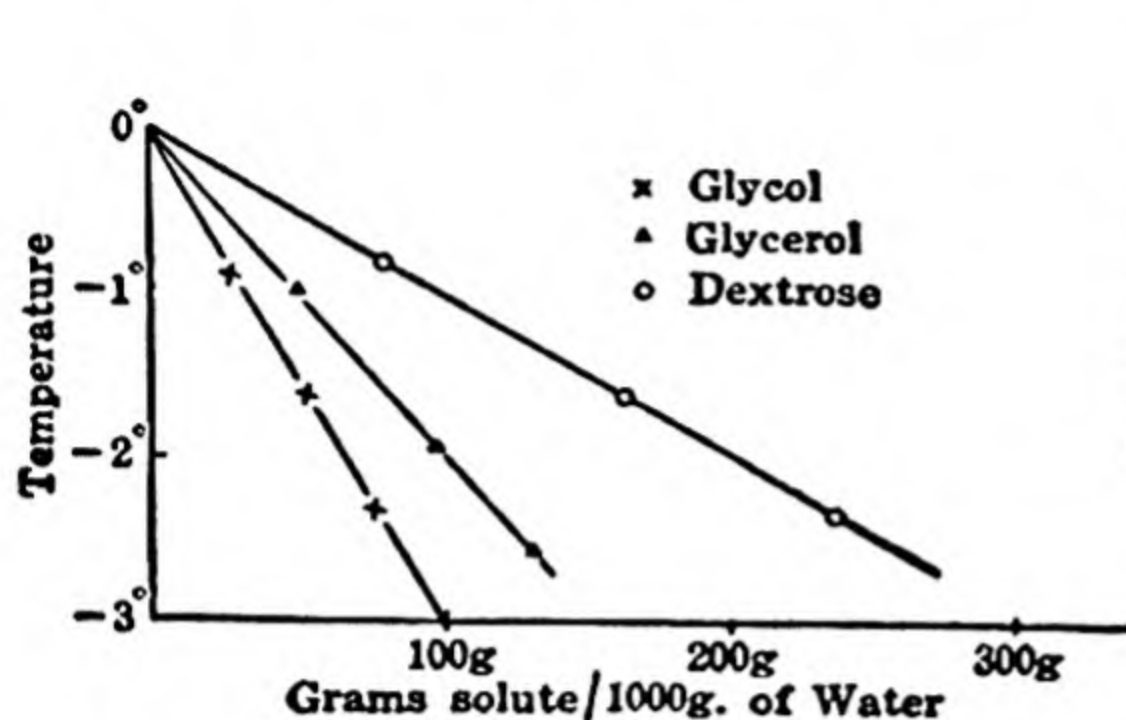
Fig. 44. Freezing Point Depression
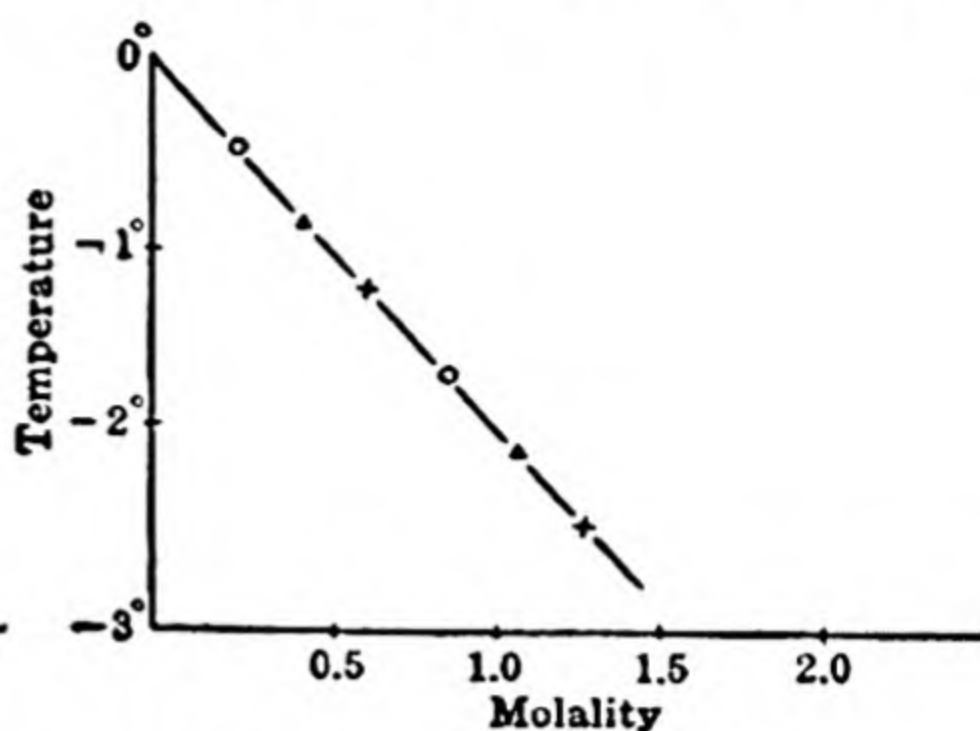
Fig. 45. Freezing Point Depression

can be shown by a single curve if the freezing points are plotted against molality. (Fig. 45.)

The freezing point of a liquid is the temperature at which the solid and liquid forms of the substance are in equilibrium at a total pressure of one atmosphere, *i.e.*, the solid and liquid phases of the substance have the same vapor pressure. The presence of the solute decreases the vapor pressure of the solvent. The solid phase, which separates from a dilute solution when it begins to freeze, is the solvent free from any of the solute. Hence, as shown in Fig. 46, the vapor pressure of liquid water from the solution is less at 0° than the vapor pressure of ice. The effect of changes in temperature on the vapor pressure of the solid is greater than on the vapor pressure of the liquid. By cooling

Fig. 46. Equilibrium of Ice with Pure Water and Solution

the solution, a temperature is reached at which the solid pure ice and the liquid solution have the same vapor pressure. *The depression of the freezing point of the solvent is proportional to the mole fraction of the solute and approximately proportional to the molality of the solution.* However, this effect is greater

than proportional to the molality in aqueous solutions of acids, basic hydroxides, and salts. The lowering of the freezing point of the solvent in a one molal solution is *the molal depression of the freezing point*. The molal depression constants of several liquids are shown in Table 8.

TABLE 8. MOLAL DEPRESSION OF THE FREEZING POINT OF SEVERAL SOLVENTS

Solvent	Freezing Point (° C.)	Molal Depression (° C.)
Water	0.00	1.86
Acetic acid	17.00	3.90
Benzene	5.40	5.12
Dioxane	11.78	4.63
Ethylene bromide	10.00	12.50
Naphthalene	80.00	6.80
Phenol	38.50	7.40
Tribromophenol	95.00	20.40

Vapor Pressures of Liquid Mixtures. Each pure liquid has a definite vapor pressure at a fixed temperature. In a solution of two liquids in each other, the vapor pressure of each liquid is decreased by the presence of the other, so that the actual pressure of the mixed vapors is less than the sum of the vapor pressures of the two pure liquids. The vapor pressure of the solution is usually intermediate between the vapor pressures of the pure liquids, but there are some liquid mixtures with lower vapor pressures than either component and others with higher vapor pressures than either component.
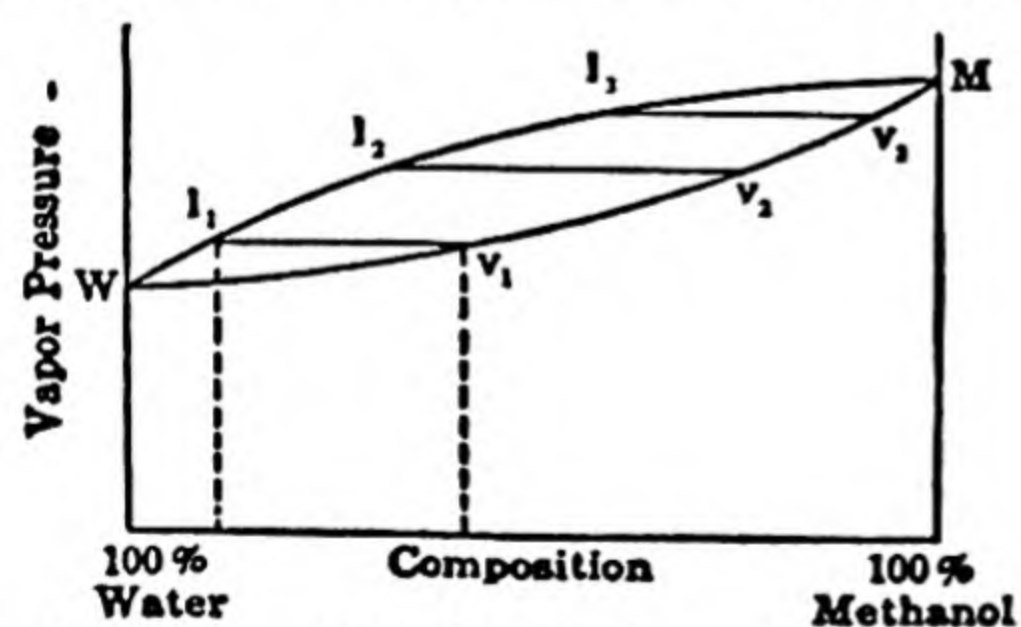
Fig. 47. *Liquid Pairs with Intermediate Vapor Pressures*

The vapor pressure composition relation of the first type is shown graphically in Fig. 47. The composition is measured along the line from 100 per cent water to 100 per cent methanol. The vapor pressure of pure water is shown by the point W and of pure methanol, by the point M. The curve WlM shows the vapor pressures of all solutions of water and methanol at constant temperature. Since vapors from solutions of this type always contain a larger proportion of the more volatile substance than contained by the

liquids with which they are in equilibrium, the composition of the vapor is shown by the curve WvM. Thus, the liquid of the composition shown by l_1 is in equilibrium with the vapor of the composition v_1, the liquid of composition l_2 is in equilibrium with the vapor v_2, and so forth.

The vapor pressure relationship for liquid pairs which yield a solution of minimum vapor pressure is shown in Fig. 48. As in the preceding type, liquids of the composition l_1 and l_2 are in equilibrium with the gas mixtures v_1 and v_2, respectively. With increasing percentages of the liquid B dissolved in A, the vapor pressure of the solution decreases as shown in the curve Al_1M, and the composition of the vapor is shown by the corresponding points on the curve Av_1M. Likewise, with increasing percentages of A in B, the vapor pressure of the solution decreases, as shown by the curve Bl_2M, and the composition of the vapor is shown by the curve Bv_2M. The lowest point on the curve, M, represents the composition and vapor pressure of the solution that has the
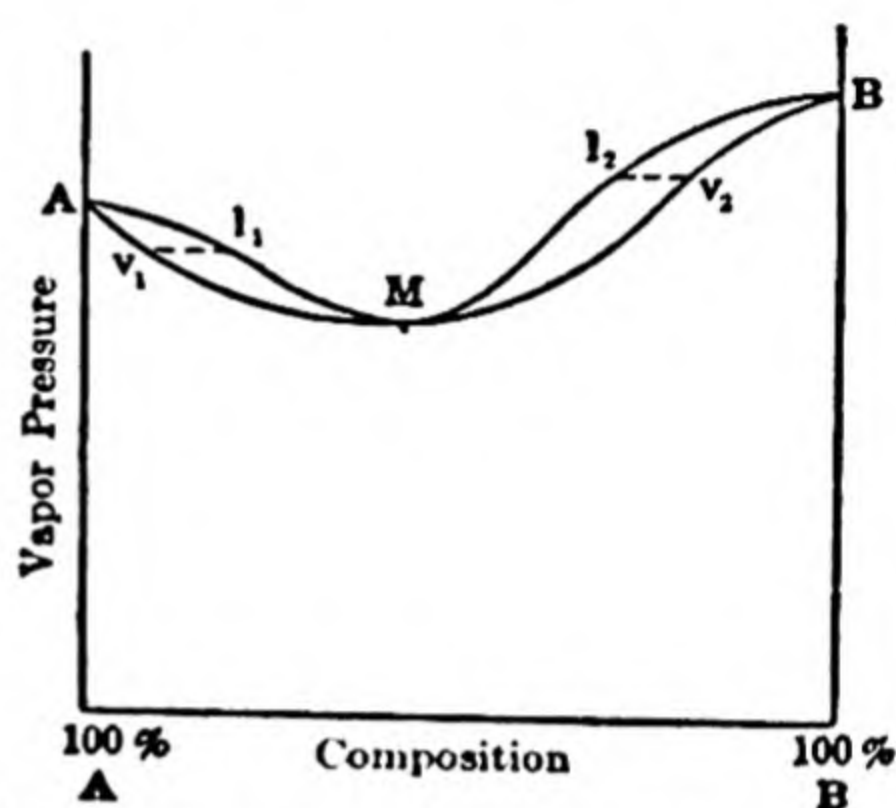
Fig. 48. Liquid Pairs with Minimum Vapor Pressure

minimum vapor pressure for this particular pair of liquids. Solutions of nitric acid and water are of this type. A third type of liquid pairs yields a solution with a greater vapor pressure than any other solution of the two liquids in each other. Grain alcohol and water form a solution possessing maximum vapor pressure.

Fractional Distillation. When a solution, composed of two volatile liquids giving intermediate vapor pressures — e.g., methanol and water — is heated, the vapor pressure of each component increases. The solution boils when the sum of the two partial pressures is equal to the atmospheric pressure. Both of the substances are present in the vapor emerging from the solution, but, as shown in Fig. 47, the vapor contains a larger proportion of the more volatile component than the liquid with which it is in equilibrium. This causes a gradual change in the composition of the solution and a corresponding change in the boiling temperature. The

vapors, boiling out of the solution between arbitrarily selected ranges in temperature, may be condensed and collected in separate containers. The first fraction contains a higher concentration of the more volatile component than found in the original solution and the last fraction a higher concentration of the less volatile component. Redistillation of the first fraction yields a fraction still richer in the more volatile material. By continuing the process of distillation and condensation in separate fractions, the liquid mixture may be separated, more or less completely, into its components. This process is known as *fractional distillation*. Liquid mixtures having vapor pressures intermediate between those of the pure components may be separated by fractional distillation. No change in the composition of either substance occurs during the fractionation of liquid pairs. A solution of the same composition as that originally distilled is obtained when all fractions are mixed together.

In practice, the separation of two substances in a liquid mixture is accomplished through the use of a fractionating column into which the vapors from the boiling solution are passed. (Fig. 49.) In this way, repeated distillations may be eliminated, and the separation may be accomplished in a single operation. Each plate in the fractionating column gives the effect of a separate distillation. The liquid that condenses in the lower part of the column is richer in the more volatile component than is the solution in the still. The vapor from this condensed liquid is likewise richer in the more volatile component than is the liquid itself. At a second plate, at a lower temperature, some of this vapor condenses and a vapor still richer in the more volatile component passes up the fractionating column. The condensed liquid flows down from the top of the

Fig. 49. Laboratory Apparatus for Fractional Distillation

column, meeting a counter current of rising vapor. Since this liquid is cooler than the gases, the less volatile material in the gas condenses. At the same time, more volatile materials in the returning liquid are evaporated. There is a continual approach toward equilibrium between liquid and vapor in the column, but the equilibrium is not attained. Eventually, the nearly pure volatile component passes from the top of the fractionating column into the condenser, while the less volatile material is returned to the still. Fractional distillation is used extensively in chemical industry as a means of separating and purifying many commercial products. The atmospheric gases may be obtained by the fractionation of liquid air, and a number of commercial products are derived by the fractional distillation of petroleum.

Constant Boiling Solutions. Liquid mixtures which have vapor pressures less than those of either pure component cannot be separated completely by fractional distillation. Such mixtures yield a solution having a minimum vapor pressure and, therefore, a maximum boiling point. During the distillation of solutions of nitric acid and water, either the acid or the water predominates in the vapor, depending on the proportion of the two substances in the solution being distilled. The boiling point gradually rises as evaporation proceeds, and in this respect the behavior is similar to that discussed in a preceding paragraph. In this solution, however, the boiling point becomes constant when the concentrations of the solution are adjusted to those of the solution having minimum vapor pressure. The distillate now has the same composition as the liquid in the distilling flask. Such solutions are *constant boiling solutions*. Repeated distillation at constant pressure does not alter the composition. The composition and boiling points of several constant boiling solutions of this type are shown in Table 9.

TABLE 9. SOME CONSTANT BOILING AQUEOUS SOLUTIONS

Solute	Boiling Point (° C.)	Per Cent of Solute in Solution
Nitric acid	120.5	68.0
Hydrochloric acid	110.0	20.2
Hydrobromic acid	126.0	47.5
Hydriodic acid	127.0	57.0
Hydrofluoric acid	120.0	35.4
Sulfuric acid	338.0	98.3

Liquid pairs which produce solutions with maximum vapor pressures also form constant boiling solutions. The constant boiling solution of this type is the solution with minimum boiling point. Ethyl alcohol and water form a constant boiling solution with minimum boiling point. The solution contains 95.57 per cent of ethyl alcohol and boils at 78.13° at a pressure of 760 mm. Solutions containing a smaller percentage of alcohol may be separated by fractional distillation into the constant boiling solution and water. The difference between the boiling point of ethyl alcohol, 78.3°, and that of the minimum boiling solution is so small that it is not practical to fractionate mixtures containing more than 95.57 per cent of alcohol, and other methods must be used for the production of 100 per cent ethyl alcohol.

Osmosis. The solution and some of the pure solvent may be placed in a container in separate layers if the difference in their densities is sufficiently great. Diffusion occurs at the boundary between these two liquid layers, and, after a time, a single solution of uniform composition is obtained. Separating the solution and the pure solvent by a partition, which permits the passage of the solvent but not of the solute, prevents diffusion from forming a single solution of uniform composition. A partition of this nature is known as a *semipermeable membrane*. A semipermeable membrane may be prepared by the precipitation of cupric ferrocyanide in the pores of an unglazed clay cup. If such a cell is filled with cane sugar solution, closed with a one-hole stopper carrying a glass tube, and placed in a beaker of pure water (Fig. 50), it is observed that the level of the liquid in the tube gradually rises. This phenomenon, osmosis, is the passage of the solvent through a semipermeable membrane from the pure solvent into the solution, or from more dilute into more concentrated solutions.
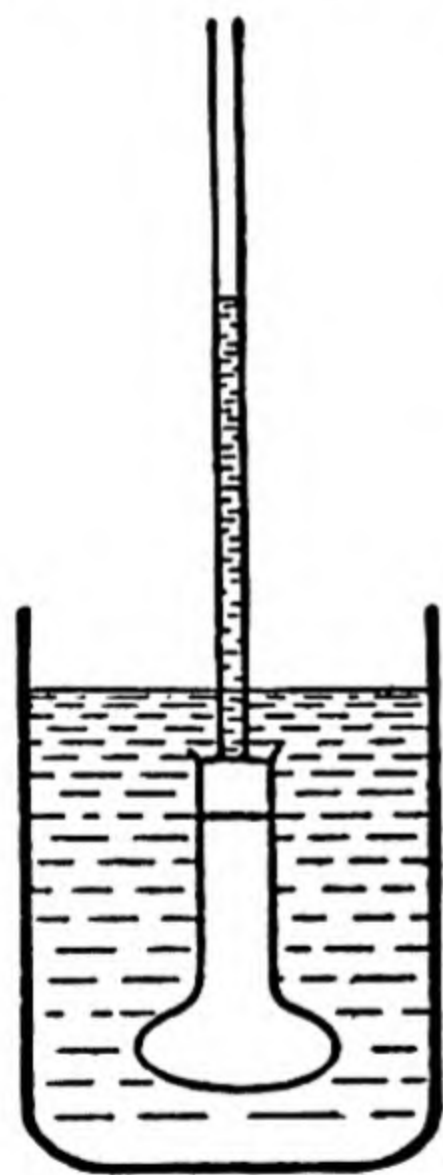
Fig. 50. Osmosis

Since the membrane is permeable to water, molecules of water may pass through the cell wall in both directions, but they enter the cell more rapidly than they emerge. Water molecules escape from the pure liquid and from dilute solutions more freely than

from concentrated solutions. This is evident from a consideration of vapor pressure relationships. A semipermeable membrane may function because of exceedingly small passages, so small that they do not permit liquids to flow but do permit the passage of gaseous molecules. In accord with this mechanism, water molecules pass more rapidly from the region of higher vapor pressures than in the opposite direction. Nonvolatile solute particles, however, remain in solution and do not pass through such membranes. There are some other ways in which the semipermeable membrane may function. Animal membranes and certain jellylike substances permit the diffusion of water, but do not allow the diffusion of the solute. In other instances the solvent may dissolve in the membrane and pass through it into the solution.

As the amount of water in the cell increases (Fig. 50), the difference in the water level builds up hydrostatic pressure. Increased pressure inside of the cell increases the rate at which water emerges. After a time equilibrium is reached, when water passes through the membrane in both directions at the same rate. No further diffusion of water into the cell can now be observed. The pressure required to establish equilibrium between a solution and the pure solvent, separated by a semipermeable membrane, is called the *osmotic pressure* of the solution. Solutions with vapor pressures proportional to the mole fraction of the solvent exhibit the same osmotic pressure in solutions of equal molality. Up to concentrations of approximately one molal, the osmotic pressure is proportional to the molality of the solution, but solutions of acids, basic hydroxides, and salts exhibit osmotic pressures greater than proportional to the molality of the solution. The osmotic pressure increases rapidly with increasing concentration. According to the measurements of Morse, the osmotic pressure of solutions of one molal concentration is approximately 25 atmospheres at 0° for solutes with vapor pressure effects proportional to the molality of the solution. The osmotic pressure increases with rise in temperature in the same manner as gas pressures increase. Solutions having the same osmotic pressure are *isotonic*.

The applications of osmosis are extensive and important. The natural membranes that surround animal and plant cells are semipermeable. Sometimes it is necessary to inject a fluid into

the blood stream of an animal. Blood is composed of corpuscles floating in a clear liquid, the plasma, a solution of various substances and has regulated concentration. The contents of the corpuscles are isotonic to the solution in which they are suspended. If pure water is introduced, the plasma is diluted and water diffuses into the corpuscles more rapidly than it emerges, building up a pressure which bursts the walls of the corpuscles. If, on the contrary, a concentrated salt solution is introduced, water diffuses out of the corpuscles more rapidly than it enters, thus rendering the corpuscles incapable of performing their natural functions. Solutions which are isotonic to the blood must be used for such injections.

Some solutes also diffuse slowly through a cell wall, and the rate of the occurrence varies for different substances. Soluble salts may pass through cell walls, but complex organic substances cannot do so. The walls of the cells in the fine roots of growing plants are freely permeable to water. Since the sap within the cells is a dilute solution, water diffuses from the soil into the cells. Passing on from cell to cell and through the channels in the plant tissue, water offsets the evaporation from the foliage. As the salts circulate through the cells of the plant, they may undergo reaction with other substances, entering into the formation of products which are stored in the cells. This contributes to the growth of the plant. Over-fertilizing the plant causes the formation of a more concentrated solution in the soil, around the roots of the plant, than is the sap within the cells. This causes the loss of water from the cells and the withering of the plant.

EXERCISES

1. What is a solution? Distinguish between solutions and suspensions.
2. What is meant by each of the following: (a) saturated solution; (b) solubility; (c) supersaturated solution; (d) molarity of a solution; (e) normality of a solution; (f) molality of a solution; (g) mole fraction?
3. What conditions affect the solubility of a solid in water? of a gas in water? What is the effect of each?
4. Explain the extraction of a solute from its solution by the use of another solvent.
5. What three properties of water are affected by nonvolatile solutes?
6. State Raoult's law dealing with vapor pressure of solutions, and explain the effects in terms of the kinetic theory.

7. What is meant by an "ideal solution"? How are deviations from Raoult's law explained?

8. What is the relation between vapor pressure depression and boiling point elevation of the solvent? Explain. What is meant by the molal elevation of the boiling point of a solvent?

9. Explain the fact that depression of the vapor pressure of a solvent also causes lowering of the freezing point.

10. Into what three groups may liquid pairs be classified on the basis of their vapor pressures?

11. What is meant by fractional distillation? Explain the separation of two liquids by distillation. What types of liquid pairs may be separated in this manner, and which may not be separated completely by fractional distillation?

12. What are constant boiling solutions? Explain the formation of a constant boiling solution during the evaporation of certain liquid pairs.

13. What is meant by osmosis? osmotic pressure?

14. Mention several applications of osmosis.

SUPPLEMENTARY READINGS

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, American Book Company, New York, 1936, chap. IV.

Briscoe, H. T., *General Chemistry for Colleges*, Houghton Mifflin Company, Boston, 1943, chap. 22.

Getman, F. H., and F. Daniels, *Outlines of Theoretical Chemistry*, John Wiley & Sons, Inc., New York, 1943, chaps. IX–X.

Chapter 8

CHEMICAL EQUILIBRIUM

Reversible processes are involved in several of the changes discussed in preceding sections of this book. Some of these are physical changes, as the evaporation of a liquid and the melting of a solid, while others are chemical, as the reaction of water vapor with iron or with carbon at high temperature. Such reactions are not normally completed unless conditions are maintained to cause the complete removal of one of the products. Consideration of such reactions is important not only to find the relative amounts of the products under specified sets of conditions but also to determine the effects caused by changing conditions. The discussion of reversible reactions, involving acids, basic hydroxides, and salts in aqueous solutions, is deferred to subsequent chapters following the study of the nature of individual particles in such solutions.

Chemical Equilibrium. If all of the reacting substances involved in a reversible reaction remain in intimate contact with one another, the system is called a *closed system.* Since two reactions of opposite effect proceed simultaneously in such closed systems, the concentrations become adjusted so that the reactions attain the same velocity. *A system is in a state of equilibrium when the reactions involved are opposite in effect and have the same velocity.* Some equilibria are homogeneous, *i.e.,* the substances are in a single phase, as in the reaction of water vapor with carbon monoxide, forming hydrogen and carbon dioxide. Equilibria are heterogeneous if two or more distinctly different phases of matter are involved, as in the reaction of carbon dioxide with calcium oxide at moderately high temperatures, forming calcium carbonate.

Many reactions not noticeably reversible under some conditions may become significantly reversible if the conditions are changed. Reactions requiring only minute concentrations of the starting materials for equilibrium are commonly considered to be com-

pleted reactions. The name reversible reaction usually signifies a system in which the two reactions reach a state of equilibrium with all of the reactants and products present in significant proportions. The double arrow may be employed to represent reversible reactions. Arrows of unequal length may be used to indicate relatively large differences in concentrations at equilibrium, the longer arrow being directed toward the substances present in higher proportions. Gaseous products may be indicated by a small arrow pointing up and precipitates by a small one pointing down. These signs are usually omitted unless gas formation or precipitation is significant in determining the extent of the reaction.

The Velocity of Reactions. The velocity of a reaction is the rate of change in the concentration or in the amount of the reacting substances. The velocity of a reaction depends on the specific nature of the substances involved, but it is affected by change in such conditions as concentration, temperature, and pressure. Such changes in conditions cause changes in the proportions of the substances at equilibrium if they affect the velocity of one reaction more than that of the other.

Effect of Changes in Concentration. The velocity of any reaction depends on the concentrations of the reacting substances. The relation between concentration and reaction velocity was stated in 1863 by Guldberg and Waage as the **Law of Mass Action or Molecular Concentrations: The velocity of a chemical reaction is proportional to the product of the molecular concentrations of the reacting substances, with each concentration raised to the power numerically equal to the coefficient of the substance in the equilibrium equation.** Molecular concentrations may be measured as molar concentrations, the number of moles in one liter. The molar concentration is usually represented by enclosing the symbol or formula, as may be appropriate, in brackets.

Through the application of the law of mass action, *an equilibrium constant* may be derived to represent the concentration relationships quantitatively. Ethanol and acetic acid react reversibly to form water and ethyl acetate, a compound known as an ester.

$$C_2H_5OH + HC_2H_3O_2 \rightleftharpoons (C_2H_5)C_2H_3O_2 + H_2O$$
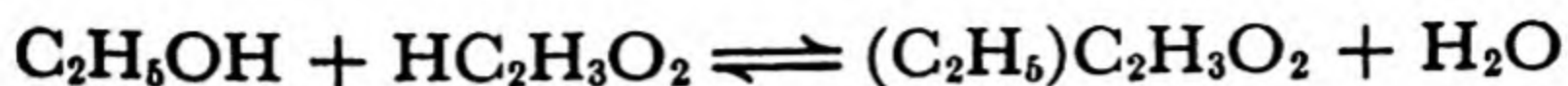
The velocity of the reaction of ethanol with acetic acid is proportional to the product of the molar concentration of the two substances.

$$V_1 \infty [C_2H_5OH] \times [HC_2H_3O_2]$$

Introducing a velocity constant k_1,

$$V_1 = k_1 \times [C_2H_5OH] \times [HC_2H_3O_2]$$

The velocity of the opposite reaction V_2 is:

$$V_2 = k_2 \times [(C_2H_5)C_2H_3O_2] \times [H_2O]$$

These velocities are equal at equilibrium:

$$V_1 = V_2$$

$$k_1 \times [C_2H_5OH] \times [HC_2H_3O_2] = k_2 \times [(C_2H_5)C_2H_3O_2] \times [H_2O]$$

$$\frac{[(C_2H_5)C_2H_3O_2] \times [H_2O]}{[C_2H_5OH] \times [HC_2H_3O_2]} = \frac{k_1}{k_2} = K \text{ equilibrium}$$

The equilibrium constant is equal to the ratio of the product of the molar concentrations of the substances formed and the product of the molar concentrations of the reactants, with each concentration raised to the power shown by the coefficient in the reaction equation. The concentrations of the substances on the right side of the equation, as written, are always in the numerator. The numerical value of this ratio is altered by changes in temperature. Starting with equivalent quantities of ethanol and acetic acid, equilibrium is established when two thirds of these substances have been converted into ethyl acetate and water. In this system the value of the constant is:

$$K = \frac{0.667 \times 0.667}{0.333 \times 0.333} = 4$$

If the proportions of ethanol and the acid are two to one, it is found that 84.5 per cent of the acid is converted into the ester. An increase in the concentration of one of the reactants causes a proportional decrease in the concentration of the other.

$$K = \frac{0.845 \times 0.845}{(2 - 0.845) \times (1 - 0.845)} = 4$$

The combination of hydrogen with iodine is an example of an homogeneous equilibrium in the gaseous state.

$$H_2 + I_2 \rightleftharpoons 2\,HI$$
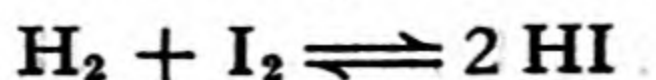
The equilibrium constant for this system is shown by the ratio:

$$K = \frac{[HI]^2}{[H_2] \times [I_2]}$$

Since this ratio is constant, any increase in the concentration of either hydrogen or iodine causes a decrease in the concentration of the other and a corresponding increase in the concentration of hydrogen iodide to maintain the constant value required for equilibrium at this temperature.

An increase in the concentration of one of the substances involved in a mixture at equilibrium causes a new state of equilibrium to be established, with an increase in the proportion of substances formed by the reaction of the added substance.

Effect of Changes in Temperature. The velocity of chemical reactions increases with rise in temperature. No generalization stating an exact relation between temperature and reaction velocity can be drawn, but, as an approximation, the velocity of many reactions may be doubled for each 10° rise in temperature. According to the kinetic theory it may be calculated that a 10° rise in temperature increases the kinetic energy of the molecules by only a small percentage. Consequently, great increases in the rate of reaction, amounting to 100–400 per cent, cannot be explained by increased numbers of molecular collision resulting from greater kinetic energy. As an explanation, Arrhenius suggested the hypothesis that only a small percentage of the molecules involved in reactions of low velocity are active enough to enter into reaction, *i.e.*, the majority of the molecular collisions do not lead to reaction. The great increase in reaction velocity accompanying a relatively small rise in temperature may be explained by the assumption that a large proportion of molecules have energies just below that required for reaction. Hence, the relative number of molecules activated sufficiently to cause reaction may increase at a much greater rate than the kinetic energy resulting from temperature change.

A rise in temperature causes both reactions involved in a reversible change to be accelerated. Consequently, a state of equilibrium is established more quickly at high than low temperatures. Nevertheless, a change in temperature does not have the same effect

on both reactions. One of the reactions involved in an equilibrium system is exothermic, and the opposite reaction is necessarily endothermic. It is observed that raising the temperature accelerates the reaction which absorbs heat more than the other. This, naturally, causes a change in the proportions of the substances at equilibrium. This effect is stated in terms of **van't Hoff's Law: If the temperature of a system in a state of equilibrium is raised, the equilibrium is disturbed so as to increase the proportions of the products of the endothermic change.** This means that the equilibrium constant is not independent of temperature.

Effect of Changes in Pressure. Changing the volume of a substance changes its concentration. This is particularly evident in the case of gaseous substances, as described more or less accurately by Boyle's law. In irreversible processes, under given conditions, the effect of change in pressure is equivalent to the concentration effect. Thus, the combustion of substances in pure oxygen takes place more rapidly than in air. The partial pressure of oxygen in the pure gas is approximately five times as great as in air at the same total pressure, because the molecular concentration is about five times as great.

The effect of change in pressure on both reactions involved in a reversible process must be considered in order to determine the effect on the system. If the change in concentration, caused by the pressure change, alters the rate of one reaction more than the rate of the other, the equilibrium proportions are necessarily altered. If the total number of gas molecules is the same in the products as in the initial substances, changes in pressure do not have a greater effect on one reaction than on the other — unless the changes are so great that the gas laws no longer apply. This may be illustrated by the reaction of hydrogen with iodine, forming hydriodic acid.

$$\frac{[HI]^2}{[H_2] \times [I_2]} = K$$

Doubling the pressure in this system doubles the concentration of each of the substances, and, therefore, does not change the ratio shown by the constant nor affect the equilibrium proportions.

Pressure change has a great effect on the system involving the decomposition of calcium carbonate.

$$CaCO_3 \rightleftharpoons CaO + CO_2 \uparrow$$
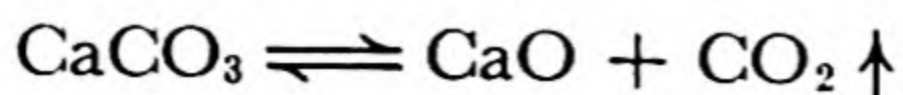
In a closed system, the pressure of carbon dioxide at a fixed temperature increases until equilibrium is established. The other two substances involved in this system are solids, and changes in external pressure have no effect on the proportions of the active material in the surfaces of these substances. Consequently, the pressure of carbon dioxide at each temperature is itself definite. At 800°, the pressure of carbon dioxide required for equilibrium is 0.22 atmosphere. Suppose that the pressure is doubled without change in temperature. It is obvious that the reaction producing calcium carbonate is accelerated by the great increase in the concentration of carbon dioxide, but the reverse reaction, the decomposition of calcium carbonate, is not affected. Equilibrium is again established when the pressure of carbon dioxide is reduced to 0.22 atmosphere. This again is merely the concentration effect.

Changes in pressure affect the equilibrium mixture in the reaction of sulfur dioxide with oxygen differently from the examples just considered.

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$$
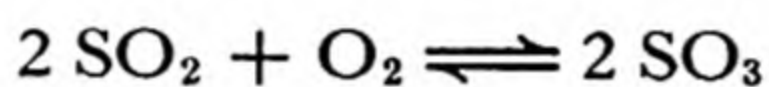
The system is homogeneous, but the number of gas molecules changes during the reaction.

$$\frac{[SO_3]^2}{[SO_2]^2 \times [O_2]} = K$$

Doubling the pressure doubles the concentration of each gas in this system, but this does not produce the same effect on the two reaction velocities. Doubling all concentrations increases the product in the denominator of the equilibrium ratio more than in the numerator. The actual ratio is, therefore, less than the constant, and the system is out of equilibrium. The velocity of the reaction of sulfur dioxide with oxygen is increased to a greater degree than that of the decomposition of sulfur trioxide. Equilibrium is restored when the two velocities have again become equal, *i.e.*, the concentrations of sulfur dioxide and oxygen have decreased and the concentration of sulfur trioxide has increased, making the actual ratio equal to the constant required for equilibrium. *If the reacting volumes of the products and of the initial substances in a reversible reaction differ, an increase in the total pressure applied to the system increases the equilib-*

rium proportions of the substances that occupy the smaller volume. The value of the equilibrium constant itself is not affected by changes in pressure, unless the pressure is great enough to cause deviations from Boyle's law for one or more of the substances involved.

Effect of Catalysts. The velocities of a number of reactions are affected by catalysts. Catalysts that cause an increased reaction velocity are accelerators, and those causing a decreased velocity are inhibitors. Some catalysts are homogeneous with the substances in the system they catalyze, while others are heterogeneous. The function of a positive catalyst is to lower the energy of activation required for the reaction, so that a larger proportion of the molecules have sufficient energy to react in the presence of the catalyst than in its absence. In many reactions, the catalytic action is due to intermediate substances formed by reactions occurring more rapidly than the direct reaction at the same temperature. These intermediate materials then decompose, producing the original catalyst and the substance for which the reaction is being carried out. In some instances, the product formed by a slow reaction may itself catalyze the reaction. Catalysts produced in this way are called *autocatalysts*. Oxides of nitrogen produced by nitrocellulose in its own decomposition may catalyze the reaction enough to cause the detonation of this substance.

Inhibitors, or negative catalysts, produce their effect in some instances by combining with positive catalysts to form relatively stable products. In the presence of urea, oxides of nitrogen formed by the slow decomposition of nitrocellulose are removed, and the explosive is stabilized enough so that it may be handled safely.

The action of heterogeneous catalysts is due to surface forces at the boundary between the substances. Such catalysts are *contact catalysts*. They are usually solids in a finely divided or spongy condition, which gives maximum surface for a specified weight of the substance. One of the surface properties, often prominent in finely divided solids, is the attraction of gases and dissolved substances, to form an extremely thin film attached to the surface. This phenomenon is called *adsorption*. Adsorption depends not only on the state of subdivision, but also on the nature of the materials. The energy of the adsorbed molecules is changed by the forces operating in these surface films. This effect causes increased rates of reaction

in many instances, although adsorption does not always lead to catalytic action.

The presence of small proportions of other substances affects the activity of catalysts. Substances which increase the activity of catalysts are called *promoters*. Some substances inhibit the action of the catalyst, probably by reacting with the surface molecules to form stable products. Such substances are known as *catalyst poisons*. Applications of these effects are involved in a great many industrial processes.

The catalyst does not exert a preferential effect on the velocity of either reaction in equilibrium, but accelerates or inhibits both equally. Consequently, the catalyst does not affect the equilibrium proportions in a system. Positive catalysts are employed frequently to cause the system to reach, or approach, equilibrium more quickly. Because of this, it is often possible to carry out a process at a lower temperature than otherwise required. If the reaction is exothermic, the use of lower temperatures, thus made possible, increases the yield of the desired product. The function of the inhibitor is, as the name implies, to decrease the rate of reaction, and thus to stabilize a product at existing temperatures.

Le Chatelier's Principle. The effects of changes in concentration, temperature, and pressure are aspects of a general principle. The principle relating all these effects on systems in equilibrium is known as **Le Chatelier's Principle: The application of a stress, *e.g.*, a change in concentration, temperature, or pressure, to a system in a state of equilibrium increases the proportions of the substances formed by the reaction tending to relieve the stress.** Increasing the concentration of one of the reactants increases the yield of the products formed by the reaction of this substance. The application of pressure increases the yield of the substances with smaller volume. Equilibrium is restored when the concentrations have been altered so that they are in accord with the constant. A rise in temperature increases the velocity of the endothermic reaction more than that of the exothermic reaction. The equilibrium constant is altered in this change, and the concentrations are correspondingly changed.

Le Chatelier's principle is applicable to all systems in equilibrium, both physical and chemical. It applies to changes in both

homogeneous and heterogeneous systems. Many applications of this principle are encountered in subsequent sections of this book.

EXERCISES

1. What is meant by each of the following: (a) reversible reaction; (b) a state of equilibrium; (c) an equilibrium constant; (d) homogeneous equilibrium; (e) heterogeneous equilibrium?
2. What is meant by the velocity of a reaction? What is the effect of changes in concentration on the velocity of reaction?
3. What is the effect of a change in the concentration of one of the substances in a system at equilibrium? Explain.
4. Formulate the expression for the equilibrium constant for the system: $H_2O + CO \rightleftharpoons CO_2 + H_2$. The equilibrium constant for this system is found to be 0.63 at 1000°. Explain this statement, and indicate a change which would increase the yield of hydrogen.
5. How is the great effect on reaction velocity caused by a relatively small rise in temperature explained?
6. State van't Hoff's law. Explain the effect of a temperature rise on the equilibrium proportions in the system: $2 NO + O_2 \rightleftharpoons 2 NO_2 + 27,800$ cal.
7. What is the effect of a change in the partial pressure of a gas in a system at equilibrium? Explain.
8. What is the effect of a change in total pressure on the following systems involving gases:

$$N_2 + O_2 \rightleftharpoons 2 NO$$
$$4 HCl + O_2 \rightleftharpoons 2 H_2O + 2 Cl_2$$
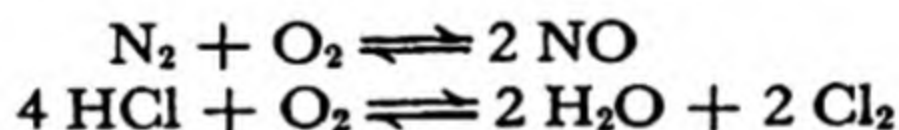
9. State the principle of Le Chatelier, and give examples to illustrate its meaning and application.
10. An equilibrium mixture in the gaseous state is represented by the following equation: $PCl_5 \rightleftharpoons PCl_3 + Cl_2 - 30,000$ cal.
    (a) Formulate the expression for the equilibrium constant
    (b) In terms of this constant, explain the effect of an increase in the total pressure; an increase in the partial pressure of chlorine
    (c) What effect has a rise in temperature on the value of the equilibrium constant?
11. What is a catalyst? What is the function of an accelerator? an inhibitor? a promoter?
12. Indicate two mechanisms by which an accelerator may function.

SUPPLEMENTARY READINGS

Hildebrand, J. H., *Principles of Chemistry*, The Macmillan Company, New York, 1930, chaps. XI–XIII.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, American Book Company, New York, 1936, chap. VII.

Getman, F. H., and F. Daniels, *Outlines of Theoretical Chemistry*, John Wiley & Sons, Inc., New York, 1943, chaps. XII–XIII.

Chapter 9

DETERMINATION OF MOLECULAR AND ATOMIC WEIGHTS

The weights of substances entering into chemical reactions are proportional to their molecular weights or to some multiple of these weights. Molecular weights are defined in preceding sections of this book, and calculations based on these weights are illustrated. The principles underlying the experimental determination of these weights have now been developed.

Molecular Weights from Formulas and Atomic Weights. The formula of a substance represents a molecular weight or a mole. Therefore, the numerical value of the molecular weight is easily obtained from the formula and the atomic weights of the constituent elements. The derivation of a simple or empirical formula of a substance from the percentage of the constituent elements has been discussed in Chapter 2, page 25. The formula shows the ratio of the atomic weights to each other, and any multiple of this ratio agrees with the percentage composition. Hence, the formula of the substance cannot be established definitely unless the molecular weight is known. There are two compounds composed of carbon and hydrogen in the ratio 7.75 per cent hydrogen and 92.25 per cent carbon. Making use of the atomic weights of these elements the simple formula is calculated:

$$7.75 \div 1.008 = 7.69$$
$$92.25 \div 12 = 7.69$$

The atomic weights of the elements in these compounds are in the ratio of one to one, and the empirical formula is CH.

The same formula cannot satisfactorily represent two compounds with notably different properties. The formula CH is not the true formula of either of the substances. The formula CH corresponds to a molecular weight of 13. The molecular weight of one of the substances is found to be 26 and that of the other 78. Therefore,

the correct formulas of the two substances are C_2H_2, acetylene. and C_6H_6, benzene, respectively. In this example, the values of the atomic weights have been taken from a table. These weights are, however, determined by experiment, and the experimental methods frequently require the knowledge of the molecular weights of compounds that contain the various elements.

Experimental Determination of Molecular Weights. The molecular weight of a substance is the weight of its molecule in units based on the atomic weight of oxygen, designated arbitrarily as 16. Molecular weights of two substances show the weight ratio of the two different kinds of molecules. The weight ratio of the molecules of two substances may be determined experimentally by weighing the same number of molecules of each substance. Since equal volumes of all gases contain an equal number of molecules at the same temperature and pressure, the weights of equal volumes of gases under such conditions are in the same ratio as the weights of the individual molecules.

One liter of oxygen at standard temperature and pressure weighs 1.429 g. and contains 2.7×10^{22} molecules. One liter of hydrogen at standard conditions weighs 0.0899 g. and contains the same number of molecules. One liter of carbon dioxide under similar conditions weighs 1.964 g. Consequently, the weights of the individual molecules of oxygen and hydrogen are in the ratio of 1.429 to 0.0899; oxygen and carbon dioxide, 1.429 to 1.964; and hydrogen and carbon dioxide, 0.0899 to 1.964. These numbers do not express molecular weights, because they are based on a weight of 1.429 for oxygen molecules, whereas the basis of molecular weights is 16 for the oxygen atom. It is now evident that two fundamental steps are necessary for the experimental determination of molecular weights, *viz.*, the determination of the weights of equal numbers of molecules of substances, and the conversion of the weights thus obtained to the standard.

Molecular Weight of Oxygen. It is necessary to find the number of atoms in the oxygen molecule in order to establish the molecular weight of oxygen. It has been shown by experiment that a given volume of oxygen reacts with twice its volume of hydrogen and that the volume of the water vapor formed is also twice the volume of the oxygen, all measurements being made at the same tempera-

ture and pressure, and that equal volumes of gases contain the same number of molecules. Therefore, the number of molecules of water is twice the number of molecules of oxygen from which it is produced. That is, each oxygen molecule is split into two equal reactive units during this reaction. Consequently, the oxygen molecule is shown to be diatomic, its molecular weight is 32, and one mole is 32 g.

Molar Volume of a Gas. One liter of oxygen weighs 1.429 g. under standard conditions of temperature and pressure. Therefore, one mole of oxygen occupies 32/1.429 or 22.41 liters under these conditions. This same volume of any other gas under standard conditions contains one mole. Hence, the volume 22.41 liters is called *the molar volume of gas.* The number of molecules in the molar volume of gas has been calculated to be 6.064×10^{23}. The weight of one liter of any gas under standard conditions may be calculated by dividing the gram molecular weight by 22.41. The density of any gas compared to air is also calculated on the basis that at 0° and 760 mm. 22.41 liters of air contain approximately 78 per cent of one mole of nitrogen, 21 per cent of one mole of oxygen, and 1 per cent of one mole of argon. Consequently, 22.41 liters of air weigh approximately 28.96 g. The density of carbon dioxide is 44/28.96, or 1.52 times the density of air.

The Molecular Weight of a Gas. The weights of equal volumes of gases are in the same ratio as their molecular weights. In a preceding paragraph it has been stated that the weights of one liter of oxygen, hydrogen, and carbon dioxide are, respectively, 1.429 g., 0.0899 g., and 1.964 g. The ratio of the molecular weight of hydrogen to 0.0899 is equal to the ratio of the molecular weight of oxygen, 32, to 1.429.

$$\frac{X}{0.0899} = \frac{32}{1.429}$$

$$X = \frac{32}{1.429} \times 0.0899 = 22.41 \times 0.0899 = 2.015 \text{ g.}$$

One mole of any gas is equal to the weight of 22.41 liters under standard conditions. One mole of carbon dioxide is equal to 22.41 × 1.964 g. or 44.01 g. Therefore, the molecular weight of carbon dioxide is 44.01. It is found by experiment that 200 ml. of a gas weigh 0.52 g. under standard conditions. One mole of this

gas is $0.52 \times 5 \times 22.41 = 58.24$ g., and the molecular weight is 58.24.

Molecular Weights of Volatile Substances. If the substance whose molecular weight is to be determined is not a gas under standard conditions, the volume of a weighed quantity of the material may be measured at a temperature and a pressure at which it is gaseous. Corrections are then made to standard conditions just as though it were a gas, and the molecular weight is calculated in the usual manner as the weight of 22.41 liters. It must be understood, however, that the weight obtained is the apparent molecular weight of the substance in the gaseous state, and it is assumed that no change in the molecular constitution of the substance occurs during its evaporation. If the substance decomposes, partially or completely, the resulting weight does not represent the true molecular weight, because the number of gaseous molecules is greater than the number of molecules in the liquid or solid state.
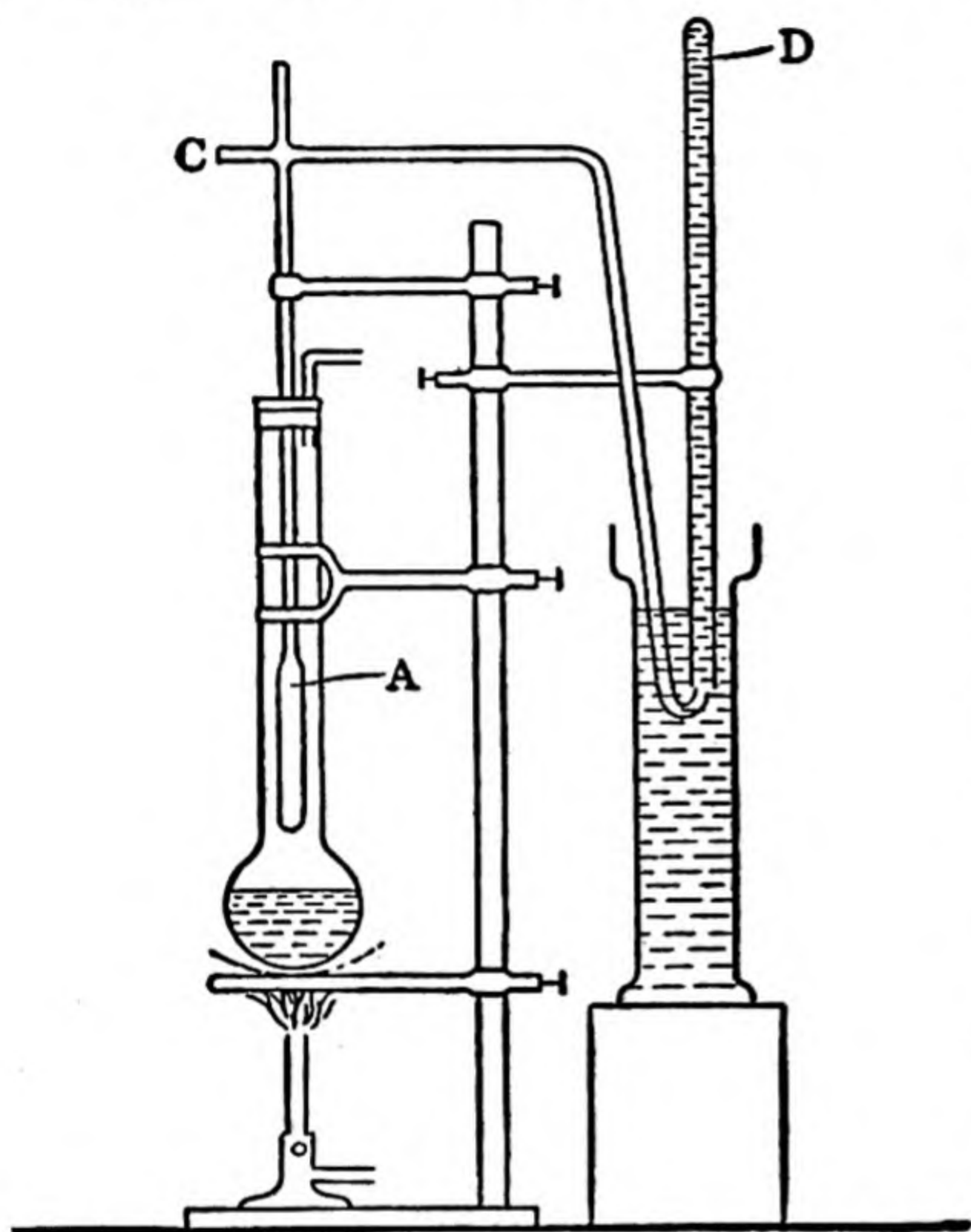
Fig. 51. *Apparatus for Victor Meyer Method*

One of the methods of determining the molecular weight of a volatile substance is the Victor Meyer method. The apparatus (Fig. 51) consists of a tube *A*, approximately 1 m. in length and 6 cm. in diameter, provided with a side tube for the collection of the evolved gases. This tube is surrounded by a jacket through which steam, or some other suitable vapor, may be passed in order to vaporize the substance whose molecular weight is to be determined. When the apparatus has come to constant temperature, the inverted tube *D*, filled with water, is placed over the end of

the delivery tube, and a small bulb containing an accurately weighed sample of the substance is caused to drop into the apparatus from the side arm C. The bulb breaks when it strikes the bottom of the tube and its contents vaporize, forcing out a volume of air equal to the volume of the vapor formed. The displaced air is collected and measured, and the temperature and pressure are noted.

The molecular weight of a volatile substance is calculated as the molecular weight of a gas. Suppose that a sample of a substance weighing 0.155 g. is vaporized, and that the displaced air, collected over water, is found to occupy a volume of 49.4 ml. at 20° and 757.5 mm. pressure.

$$\text{Gas pressure} = 757.5 - 17.5 = 740 \text{ mm.}$$

$$\text{Volume (at 0° and 760 mm.)} = 49.4 \times \frac{273}{293} \times \frac{740}{760} = 44.8 \text{ ml.}$$

$$\text{Weight of 44.8 ml.} = 0.155 \text{ g.}$$

$$\frac{X}{0.155} = \frac{22410}{44.8}$$

$$X = 0.155 \times \frac{22410}{44.8} = 77.5 \text{ g.}$$

One mole of this substance is 77.5 g., and the molecular weight is 77.5 according to this experiment.

Molecular weight determinations usually are not highly accurate, but they are close enough to show which multiple of the weight corresponding to the empirical formula is the true molecular weight. In this manner, the true formula is established from analytical data. The empirical formula for a certain hydrocarbon is CH. The molecular weight is approximately 77.5. The molecular weight of the substance is a multiple of 13, the weight corresponding to the empirical formula. Clearly, the correct multiple is six, and the true molecular weight, 78. Hence, the formula of this substance is C_6H_6.

Molecular Weights of Substances in Solution. There are a number of substances with molecular weights that cannot be determined by the method outlined above. Some substances cannot be volatilized readily, and others decompose when heated. The determination of the molecular weights of such substances must be based on other effects caused by equal numbers of molecules.

The vapor pressure effect serves as the basis for the determination of the molecular weights of many substances in solution. According to Raoult's law, the mole fraction of different solutes is the same if they cause the same vapor pressure lowering when dissolved in an equal quantity of a given solvent (see page 115). If the molecular weight of one such solute is known, the others may be calculated. Such methods may be used only in solutions to which Raoult's law is applicable.

Temperature changes may be measured more easily than changes in vapor pressure. Methods for the application of this principle to molecular weight determinations usually involve measurement of the freezing point depression or of the boiling point elevation. A solution containing weighed amounts of the solute and solvent is placed in the inner tube of the apparatus, shown in Fig. 52. The tube is placed in a freezing mixture, and the temperature, at which the solid is in equilibrium with the solution, is measured before enough of the solvent has frozen to change the concentration significantly. The molal depression of the freezing point for the solvent is determined by the use of a solute of known molecular weight. Suppose that 1.5 g. of a solid, dissolved in 100 g. of water, cause a freezing point depression of 0.465°. A mole is the number of grams of the solute in 1000 g. of water required to cause a freezing point depression of 1.86°.

Fig. 52. Apparatus for Freezing Point Method

$$1.5 \text{ g. in } 100 \text{ g. of water} = 15 \text{ g. in } 1000 \text{ g. of water}$$

$$\frac{X}{15} = \frac{1.86}{0.465}$$

$$X = \frac{1.86}{0.465} \times 15 = 60 \text{ g.}$$

One mole of this solute is 60 g., and the molecular weight is 60.

Atomic Weights from Molecular Weights of Compounds. The atomic weight of an element is the average weight of its atoms

related to the weight of the oxygen atom as 16. According to the atomic theory, the atom is the chemical unit of an element, and the molecules of compounds contain integral numbers of atoms of the constituent elements. The number of atoms in one gram atom is the same as the number of molecules in one mole, because both of these quantities are based on the same unit. Consequently, a mole of any compound contains at least one gram atom of each element in the compound, but a mole may contain more than one gram atom of each element. If many compounds of some specified element are investigated, one or more of these is likely to contain only one gram atom per mole. *The gram atom of an element is the smallest weight of that element in one mole of any of its compounds.*

The first step in the experimental determination of the atomic weight of an element by this method is to find the weight of one mole of several of its compounds. The second step is to analyze the compounds and calculate the weight of the element under consideration in one mole of each compound. These weights are in each instance equal to the gram atom or to some multiple of the gram atom of the element. The third step is to select the smallest of these weights as the probable value of the approximate atomic weight. It is possible that the smallest weight so found may itself be a multiple of the atomic weight. The data for a number of compounds of chlorine are listed in Table 10.

TABLE 10. COMPOSITION OF SOME COMPOUNDS OF CHLORINE

Compound	Gram Molecular Weight	Per Cent of Chlorine	Grams of Chlorine in 1 Mole
Hydrochloric acid	36.2	97.3	35.2
Carbonyl chloride	99.6	71.8	71.5
Chloroform	119.0	89.1	107.0
Phosphorus trichloride	138.2	76.7	106.0
Phosphorus pentachloride	209.4	85.1	178.2
Methyl chloride	50.8	70.3	35.7
Carbon tetrachloride	154.8	92.2	142.7
Ethyl chloride	64.2	55.0	35.3
Sulfur monochloride	135.5	52.6	71.4
Aluminum chloride	133.1	79.8	106.2

Inspection of the data shows that the average value of the gram atom of chlorine, as found by this method, is about 35.4 g. Hence, the atomic weight of chlorine is approximately 35.4 on the oxygen

basis. The values obtained by the examination of different compounds are not identical because of errors inherent in the method. The molar weights from which the gram atoms are calculated are not themselves accurate.

Approximate Atomic Weights from Specific Heats. According to the **Rule of Dulong and Petit: The product of the specific heat and atomic weight of each solid element is approximately equal to a constant.** That is, the number of calories of heat required to raise the temperature of one gram atom of any solid element one degree is approximately the same. The average value at 20° is 6.4. But this rule is not applicable to four elements with atomic heat capacities differing greatly from the average, *viz.*, carbon, boron, silicon, and beryllium. This rule affords a basis for the determination of approximate atomic weights of solid elements. The specific heat of iron at 20° is 0.107 calorie per gram, and the approximate atomic weight of iron, according to this rule, is:

$$6.4 \div 0.107 = 60$$

The atomic weights arrived at by the application of this rule are likely to be inaccurate. They are useful, however, as a step in determining the accurate values of the atomic weights of elements producing few volatile compounds.

Accurate Atomic Weights. An element's equivalent weight expresses its reacting weight according to a standard that is one half of the atomic weight of oxygen. The reacting weights of two elements depend on the relative numbers of atoms involved and on the weights of the atoms. Hence, the weight of the atom of an element bears an integral relation to the equivalent weight. The valences of the elements depend on the numerical ratio in which the atoms react. The atomic weight of an element is the product of the equivalent weight and the valence in the compound on which the equivalent weight is based. Equivalent weights may be determined with a high degree of accuracy. The approximate value of the atomic weight is used to show which multiple of the equivalent weight must be selected as the atomic weight. Suppose that the smallest weight of sulfur in one mole of its compounds is found to fall in the range between 31 g. and 33 g., and that the equivalent weight, derived from the investigation of a number of sulfates,

is 5.3433. The equivalent weight must be multiplied by 6 to give the atomic weight.

$$5.3433 \times 6 = 32.06$$

Six is the only integral multiple of 5.3433 that gives a product agreeing with the fact that the atomic weight lies between 31 and 33. The equivalent weight of iron is found to be 27.92 by the analysis of ferrous salts. The approximate atomic weight, by the specific heat method, is 60. Hence, the true atomic weight is the integral multiple of 27.92 nearest to 60.

$$27.92 \times 2 = 55.84$$

The atomic weight of iron is 55.84, and the valence of iron in the ferrous compounds is 2.

EXERCISES

1. Why is the determination of the molecular weight necessary to establish the true formula of a compound?
2. State the two principles applied in experimental methods used for the determination of molecular weights.
3. Cite the proof that the molecular weight of oxygen is 32.
4. Explain the fact that the molar volume of all gases at standard temperature and pressure is 22.41 liters.
5. What data are required for the calculation of the molecular weight of a gas or easily volatilized substance?
6. Explain the fact that determination of the weight of 22.41 liters of gas produced by heating a liquid, after taking into account corrections for temperature and pressure, does not always give the molecular weight of the substance.
7. Explain the determination of the molecular weight of a solute by the freezing point depression it causes.
8. Why is this method not applicable to the determination of the molecular weights of all solutes?
9. Define atomic weight in terms of (a) the oxygen standard, (b) the molecular weights of compounds, (c) the relation to the equivalent weight.
10. Why is it necessary to determine the approximate value of the atomic weight of an element, since the accurate value is a multiple of the equivalent weight?

Chapter 10

THE ALKALI METALS AND HYDROXIDES

The classification of the elements into groups is mentioned in Chapter 4, page 55. The first of these groups contains the elements *lithium, sodium, potassium, rubidium, cesium.* These elements are metals which have similar properties and reactions. They are called *alkali metals* because their hydroxides are highly soluble substances, which show to a marked degree the properties characteristic of the basic substances. These metal hydroxides are known as *alkalies.* The compounds of the alkali metals with nonmetals and nonmetal radicals are salts. Sodium and potassium are the most abundant and important members of this group. The description of the salts of these metals is deferred to Chapter 25.

Occurrence of the Alkali Metals. These metals do not occur naturally in the free condition, but their compounds are widely distributed. The average relative amounts of sodium and potassium in the igneous rocks in the outer ten-mile layer of the solid earth are estimated to be 2.85 per cent and 2.60 per cent, respectively. The percentage of the other alkali metals is very small. Sea water contains approximately 2.8 per cent of sodium chloride and slightly less than 0.1 per cent of potassium chloride. Consequently, these salts are found in deposits resulting from the evaporation of sea water, and the chlorides are the most important natural sources of these metals and of their compounds. The carbonates, sulfates, and nitrates of both of these metals are found in the soil and in water and salt deposits in various parts of the world. The sodium salts of each class occur more abundantly. Sodium and potassium compounds are present in plants, sodium compounds being more abundant in sea plants and potassium compounds in land plants. The metals occur extensively in their silicates. Potassium feldspar, $KAlSi_3O_8$, is a component of granite. Lithium occurs in complex phosphates and silicates and cesium in complex silicates. Small

percentages of cesium and rubidium chlorides are found in some spring waters and salt deposits.

Preparation of the Alkali Metals. Sodium is the only one of the alkali metals which is used industrially in large quantities. It was first prepared in 1807 by Davy by the electrolysis of sodium hydroxide. An industrial method for the production of sodium by electrolysis of fused sodium hydroxide was developed by Castner in 1890. At present the most important method for the production of sodium in the United States is the electrolysis of fused sodium chloride. This process has the advantage that it employs a naturally occurring raw material instead of a substance produced from the natural materials. A second advantage is in the more efficient use of the electric current. Sodium is the only product set free at the cathode during the electrolysis of fused sodium chloride, but both sodium and hydrogen are discharged by the electrolysis of the fused hydroxide, and 50 per cent of the current is used in the liberation of hydrogen.

In the *Downs cell* for the production of sodium by electrolysis of fused sodium chloride (Fig. 53) the container is made of iron
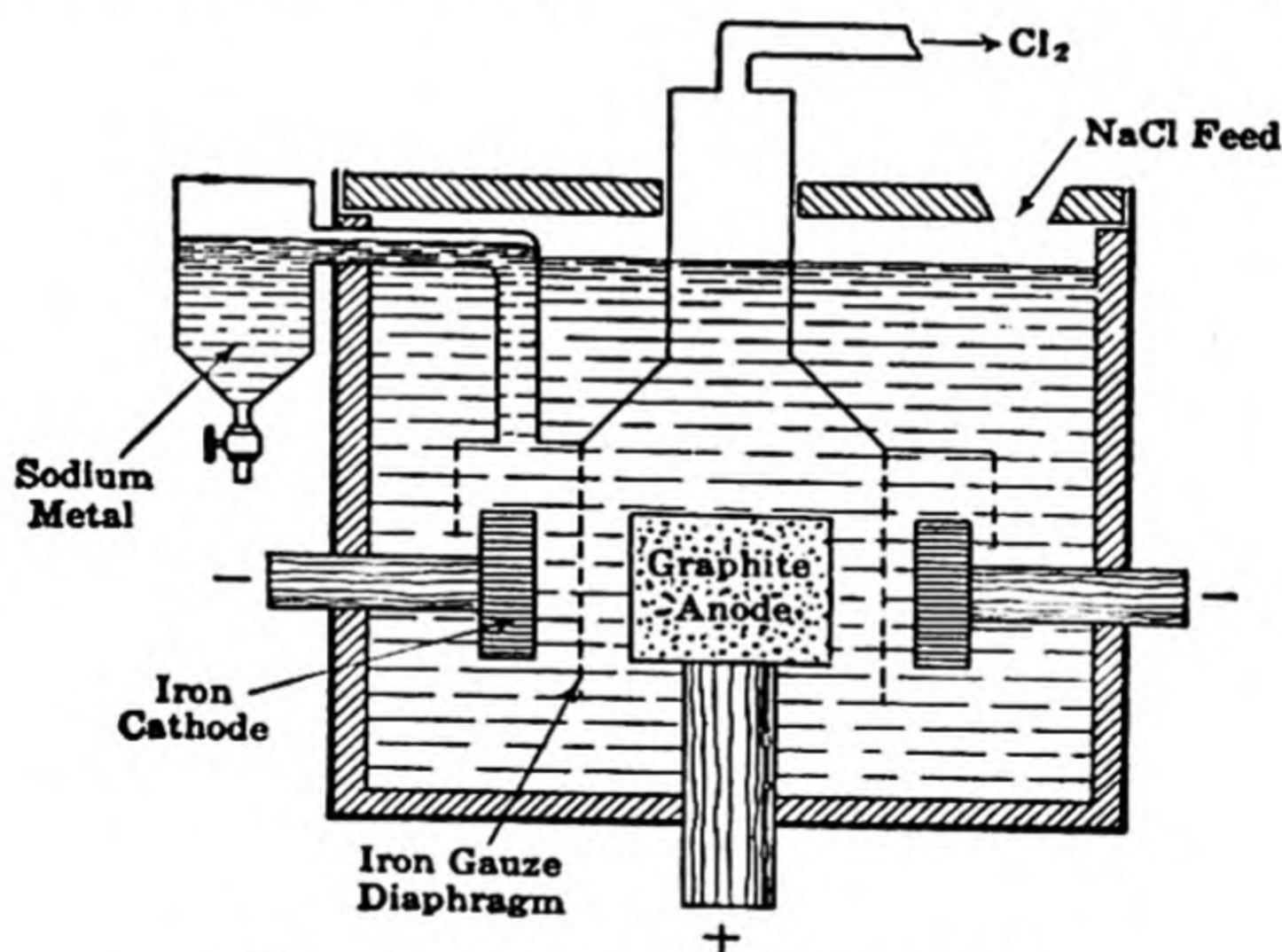
Fig. 53. Diagram of a Downs Cell

lined with firebrick. The graphite anode projects into the cell from the bottom, and the cathode is in the form of an iron cylinder around the end of the anode. An iron gauze diaphragm, separating the anode and cathode compartments of the cell, is connected to a

dome in which chlorine collects. Sodium is liberated at the cathode, fills the riser pipe, and flows out into the receiver. The fused sodium chloride is introduced from time to time through a hole in the cover of the cell. Chlorine, produced at the anode as a by-product, is stored in cylinders for industrial use. The temperature at which the cell operates, about 600°, is maintained by the passage of the current.

The other metals in this group may be prepared by the same general procedure, the electrolysis of the fused chloride or the fused hydroxide.

Properties of the Alkali Metals. The metals are soft and have relatively low melting points and boiling points. They also have low densities; lithium, sodium, and potassium being less dense than water. The untarnished surfaces of these metals have a silvery white luster, but they rapidly tarnish and lose their lustrous appearance. The metals are usually stored beneath the surface of a protecting oil so as to exclude air. When they are stored in this way, they usually do not have a metallic appearance because of a surface coating. A few of the properties of the metals of the group are listed in Table 11.

TABLE 11. PROPERTIES OF THE ALKALI METALS

Property	Lithium	Sodium	Potassium	Rubidium	Cesium
Atomic weight	6.94	23.00	39.10	85.48	132.91
Melting point (° C.)	186.0	97.5	62.3	38.5	28.5
Boiling point (° C.)	1609.0	880.0	760.0	700.0	670.0
Density, g. per ml. at 20°	0.53	0.97	0.86	1.48	1.90
Heat of formation of chloride, cal.	97,420	98,360	104,300	104,970	106,480

Reactions of the Alkali Metals. The alkali metals react vigorously with a number of the nonmetals, forming binary products, e.g., with chlorine to form chlorides, with bromine to form bromides, and with sulfur to form sulfides. The following equations are examples of a series of reactions shown by the members of this group.

$$2\,Na + Cl_2 \longrightarrow 2\,NaCl$$
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$
$$2\,Na + S \longrightarrow Na_2S$$
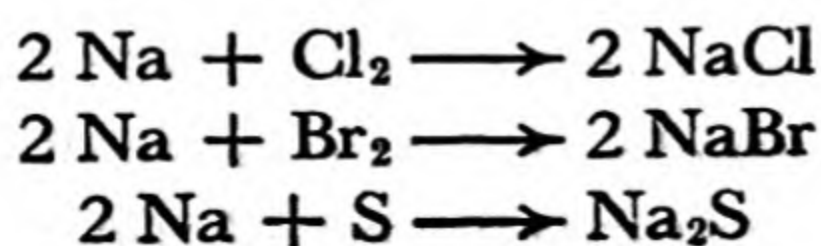
Reacting with oxygen, lithium yields the simple oxide but sodium yields the peroxide unless the temperature is kept relatively low.

$$4\,Li + O_2 \longrightarrow 2\,Li_2O$$
$$2\,Na + O_2 \longrightarrow Na_2O_2$$
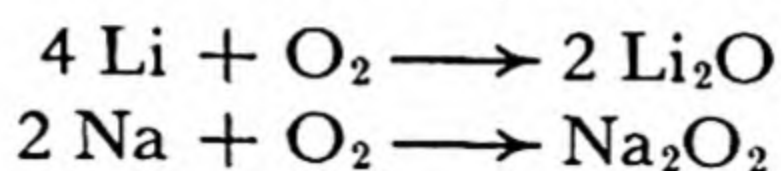
They combine with hydrogen to produce unstable hydrides in which hydrogen has a valence of $1-$. The alkali metals react vigorously with water, producing gaseous hydrogen and the hydroxide of the metal in solution. Potassium, rubidium, and cesium develop enough heat in this reaction to ignite the liberated hydrogen.

$$2\,Na + 2\,H_2O \longrightarrow H_2 + 2\,NaOH$$
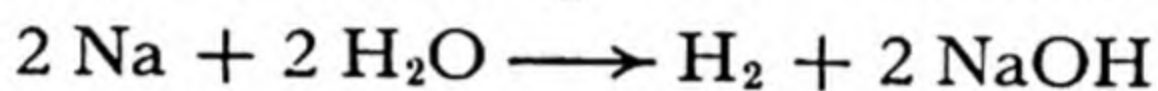
They also displace hydrogen from acids, but the reaction is too violent to be important.

The alkali metals enter into similar varieties of reactions but differ in their activities. When they are arranged in order of their atomic weights, it is found that, in general, each is more active than those that precede it in the list. Lithium is irregular in its activity relationships, and it does not resemble the other metals in the group as closely as these resemble one another. Large amounts of heat are evolved in many of the reactions of these metals. The number of calories per mole of the chloride produced is shown for each of these metals in Table 11, and it is observed that the amount is greatest for cesium.

Uses of the Alkali Metals. The most important uses of sodium are now in the production of sodium peroxide, sodium cyanide, and a number of organic compounds, such as tetraethyl lead used in gasoline. Sodium forms an alloy with mercury with the evolution of large amounts of heat. *An alloy* is a solid material containing two or more metals in intimate mixture or in combination with each other. Alloys are usually formed by dissolving the metals in each other in the molten state, and then allowing the melt to cool and solidify. An alloy in which mercury is one of the components is called an *amalgam*. The reactions of sodium amalgam are less vigorous and, consequently, more easily controlled than corresponding reactions employing metallic sodium alone. Hence, the amalgam is used in preference to the pure metal for many purposes. An alloy of lead and sodium is used in the production of tetraethyl lead. Accurate figures are not available on the industrial uses of sodium

in the past few years, but the quantity runs into thousands of tons annually.

The fact that metal atoms may emit electrons is discussed in Chapter 13. The electron, "the natural unit of electricity," is a minute particle having a negative charge. A stream of electrons flowing from one place to another is an electric current. Atoms of the alkali metals are activated by light, emitting electrons more readily than in the dark. On the basis of this property, sodium and lithium, and cesium to a small extent, are used in photoelectric cells. The surface of an electrode in a cell, from which air has been removed as completely as possible, is coated with a thin film of the metal. The gap between the electrodes is made just great enough to prevent the flow of electrons when the cell is connected in a circuit at the proper voltage and the electrodes are protected from light. Under such conditions the current cannot flow through the circuit. When light is allowed to fall upon the coated electrodes, the metal is activated sufficiently to cause electrons to flow across the gap between the electrodes, thus completing the circuit. The photo-electric cell has many important applications.

An important, though limited, use of sodium is in sodium vapor lights, in highway illumination for instance. The lamps are made with an elongated inner bulb containing the electrodes. A small amount of sodium is placed in the bulb which also contains argon under low pressure. An outer glass cylinder serves to minimize the loss of heat. The current is conducted by the argon gas at first, and enough heat is developed to vaporize sodium. Sodium vapor then conducts and emits a yellow glow which is very efficient for general illumination.

THE OXIDES AND HYDROXIDES

Oxides and hydroxides of all alkali metals may be prepared. They are strongly basic substances, which show vigorously the reactions characteristic of these classes of compounds (see Chapter 4). Sodium peroxide and the hydroxides of sodium and potassium are the only compounds of these classes that have extensive commercial uses.

Sodium Peroxide. Na_2O_2. This substance is prepared by heating metallic sodium in a current of dry air, free from carbon dioxide,

at a temperature of approximately 300°. At lower temperatures, the normal oxide Na_2O is formed. Sodium peroxide contains the peroxide radical which has a valence of $2-$. Sodium peroxide reacts with water to form hydrogen peroxide and sodium hydroxide.

$$Na_2O_2 + 2 H_2O \longrightarrow H_2O_2 + 2 NaOH$$
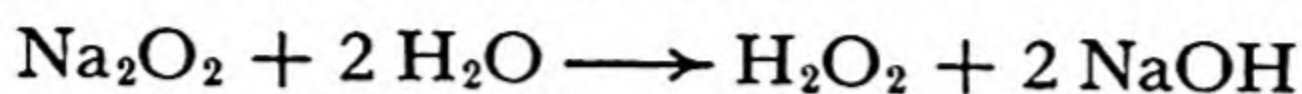
If only a small proportion of water is used, hydrogen peroxide decomposes, and oxygen is evolved.

$$2 Na_2O_2 + 2 H_2O \longrightarrow 4 NaOH + O_2$$
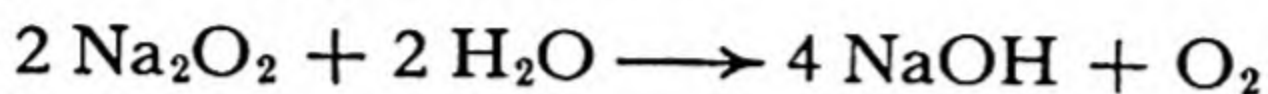
Sodium peroxide is used as a source of hydrogen peroxide and, to a limited extent, of oxygen.

Preparation of the Hydroxides of Sodium and Potassium. These substances are prepared by the same general methods, *viz.*, the electrolysis of aqueous solutions of the chloride and the reaction of the carbonate with lime, calcium hydroxide. These hydroxides may be used interchangeably for many purposes. Sodium hydroxide, being cheaper, has more extensive uses than potassium hydroxide.

The Lime-Soda Method. The reaction of sodium carbonate in solution with calcium hydroxide is a double decomposition reaction. The low solubility of calcium carbonate causes the reaction to proceed in a satisfactory manner, leaving sodium hydroxide in solution.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + 2 NaOH$$
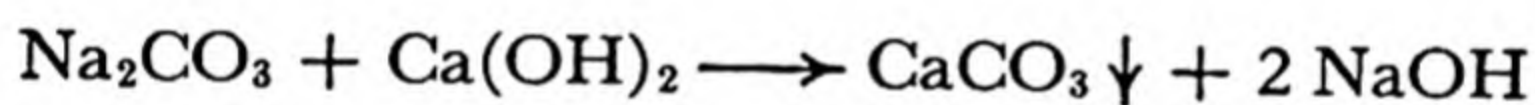
Calcium hydroxide is only moderately soluble, so that only a small concentration of this substance remains in solution at the end of the reaction. In order to produce sodium hydroxide by this method, sodium carbonate solutions are boiled with a suspension of calcium hydroxide in iron pots. As the calcium hydroxide in solution reacts and calcium carbonate precipitates, additional quantities of calcium hydroxide dissolve, keeping the solution saturated with this substance. After all of the sodium carbonate in the solution has reacted, the solids are allowed to settle, and the clear solution containing sodium hydroxide is drawn off and evaporated.

The Electrolytic Process. The passage of a direct current of electricity through a solution of sodium chloride causes the discharge of hydrogen at the cathode with the formation of sodium

hydroxide in the solution. Gaseous chlorine is produced at the anode. Chlorine reacts with sodium hydroxide. To prevent this, it is necessary to use a special type of cell in which the products do not become mixed. A number of different cells have been invented for this purpose but they operate on the same principle. The Nelson cell, represented diagrammatically in Fig. 54, is one of the cells used extensively for the industrial production of sodium hydroxide by electrolysis of sodium chloride solutions. Chlorine is a coproduct of sodium hydroxide. The anodes are graphite rods which extend down into the cell from the top. The cathode is a perforated steel shell which divides the cell into two compartments. A layer of asbestos cloth at the inner surface of the cathode permits the solutions to seep through, but prevents the mixing of chlorine with the products formed at the cathode. The asbestos cloth serves as a porous diaphragm, which permits the directed migration of the dissolved particles of the salt under the influence of the electric charges on the electrodes. The brine solution is kept at a constant level in the anode compartment by automatic feed control. During the operation of the cell, chlorine is produced at the anode and passes out of the cell through an outlet at the top of this compartment. Chlorine is dried, liquefied, and stored in cylinders unless used directly. Hydrogen is discharged at the cathode and passes out of the cell through an outlet from the outer compartment. The solution, seeping through the porous asbestos diaphragm, drips from the perforated cathode into a catch basin. This solution

Fig. 54. Diagram of a Nelson Cell

contains 8–10 per cent of sodium hydroxide and 14–16 per cent of sodium chloride. It is partially evaporated to separate most of the sodium chloride, which is much less soluble than sodium hydroxide. After the removal of the crystalline salt, the evaporation of the water is completed. The final temperature is above the melting point of sodium hydroxide, so the molten residue is allowed to cool and solidify. The solid may contain a fairly large percentage of common salt and must be further purified if the uses for which it is intended require the pure product. For most of the commercial uses of sodium hydroxide, the presence of salt is not objectionable.

The production of sodium hydroxide in the United States in 1943 is estimated * at approximately 1,715,000 tons, an increase of 13 per cent over the production in 1942. The increased production was largely due to war time demands for chlorine, and the industrial uses of sodium hydroxide did not increase correspondingly. Approximately 61 per cent of the sodium hydroxide in 1943 was produced by the electrolytic process.

Properties of the Hydroxides of Sodium and Potassium. These substances are white solids, which are highly soluble in water and absorb moisture from air. They melt at moderate temperature; sodium hydroxide at 318° and potassium hydroxide at 360°. In the preparation of these substances a molten residue, free from water, is obtained by evaporation. This material may be poured into molds and allowed to solidify. The hydroxides frequently appear on the market in the form of sticks or pellets.

Reactions of the Hydroxides of Sodium and Potassium. Solutions of these substances enter vigorously into the characteristic reactions of metal hydroxides with acids and with acidic oxides.

$$2\,NaOH + H_2SO_4 \longrightarrow 2\,H_2O + Na_2SO_4$$
$$2\,KOH + SO_3 \longrightarrow H_2O + K_2SO_4$$
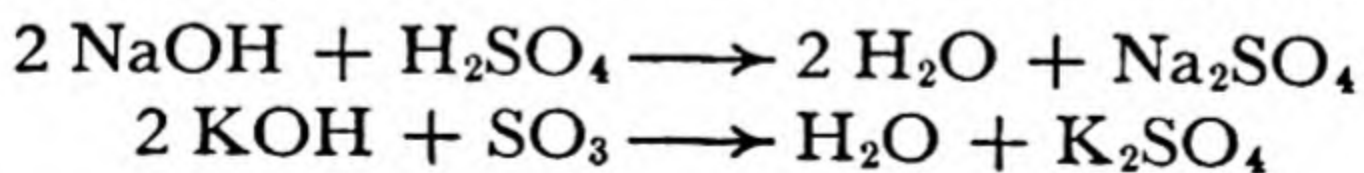
Glass bottles containing solutions of these hydroxides slowly become etched, due to reaction of the hydroxide with acidic components of the glass, such as silicon dioxide.

$$2\,NaOH + SiO_2 \longrightarrow H_2O + Na_2SiO_3$$
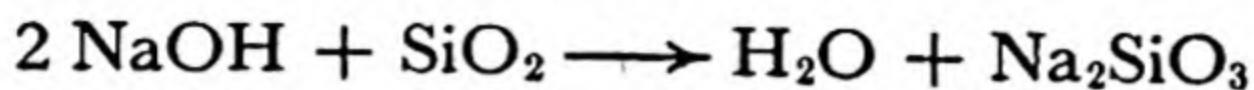
The hydroxides absorb carbon dioxide unless they are kept out of contact with air containing this gas. These hydroxides react with

* *Chem. Met. Eng.* **51,** 2, 112 (1944).

ammonium salts to form ammonia gas and with soluble salts of metals that yield slightly soluble hydroxides.

$$2\,NaOH + (NH_4)_2SO_4 \longrightarrow 2\,NH_3 \uparrow + 2\,H_2O + Na_2SO_4$$
$$2\,KOH + MgCl_2 \longrightarrow Mg(OH)_2 \downarrow + 2\,KCl$$
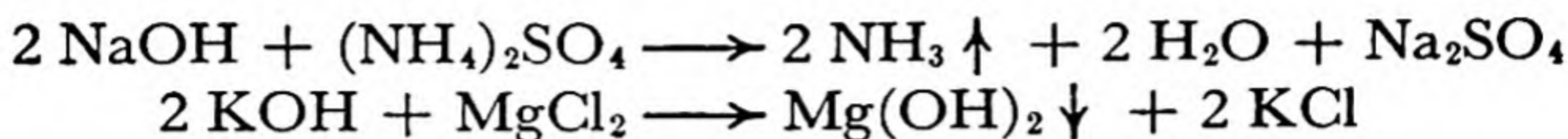
Strongly basic metal hydroxides react with some of the active nonmetals. A mixture of the chloride and hypochlorite is formed by the reaction with chlorine.

$$Cl_2 + 2\,KOH \longrightarrow H_2O + KCl + KClO$$
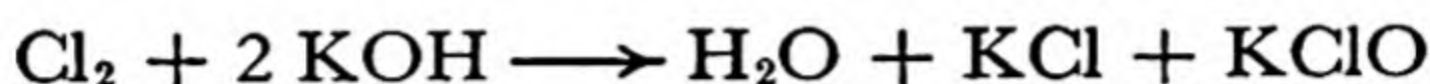
The hydroxides of sodium and potassium are known as *caustic alkalies* because of their corrosive action on animal matter.

Uses of the Hydroxides of Sodium and Potassium. Sodium hydroxide is the cheapest of the highly soluble active metal hydroxides. It is extensively used in the soap, rayon, paper, and leather industries, in the production of chemicals, in refining petroleum and reclaiming rubber, and in a number of other industries. The most extensive use of potassium hydroxide is in the production of soft soap, composed of compounds with higher solubilities than the corresponding sodium compounds. An important laboratory use of potassium hydroxide is for the absorption of moisture and carbon dioxide from air passed in contact with it.

EXERCISES

1. Discuss the occurrence of sodium and potassium and explain why potassium compounds are more expensive than corresponding sodium compounds.
2. What method is employed for the production of the alkali metals? Why is this method selected in preference to the reduction of the oxide?
3. Write equations which illustrate common reactions of the alkali metals.
4. List several important physical properties which characterize these metals.
5. What relationships are apparent when the alkali metals are arranged in the order of their atomic weights?
6. Explain the use of sodium in photoelectric cells and in sodium vapor lights.
7. How is sodium peroxide prepared? Indicate its importance.
8. Describe the preparation of the hydroxides of sodium and potassium by two different methods.
9. Write equations to represent reactions which are characteristic of active basic hydroxides.
10. Discuss the importance of the hydroxides of sodium and potassium.
11. What is the meaning of the following new terms encountered in this chapter: alkali, alkali metal, caustic alkali, alloy, amalgam?

SUPPLEMENTARY READINGS

Weeks, M. E., *The Discovery of the Elements*, Journal of Chemical Education, Easton, Pa., 1935, pp. 117–26.

Creighton, H. J., and W. A. Koehler, *Electrochemistry*, John Wiley & Sons, Inc., New York, 1935, Vol. II, pp. 255–62; 275–310.

Badger, W. L., and E. M. Baker, *Inorganic Chemical Technology*, McGraw-Hill Book Company, Inc., New York, 1941, chap. VII.

Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940, chap. IV.

Mellor, J. W., *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Company, New York, 1922, Vol. II.

Chapter 11

THE HALOGENS AND HYDROHALIC ACIDS

In the preceding chapter a natural group of active metals, the alkali metals, has been discussed. By way of contrast, this chapter deals with a group of active nonmetals providing an entirely different series of reactions, so greatly different that they exhibit an opposite type of behavior. Thus, the two groups supplement each other in illustrating the nature of chemical elements, affording a basis for understanding the system used for the classification of the elements and supplying descriptive material which will serve as a background for theories on the structure of the atoms.

The halogens are a closely related group of elements. (Shown in the seventh column of Table 3 on page 55.) The members of this group are *fluorine, chlorine, bromine,* and *iodine.* The name halogen, meaning salt-former, is based on the fact that the halogens yield a series of binary salts with the metallic elements. These nonmetals exhibit similar reactions and produce similar compounds. Their common valence is $1-$ in most of their binary compounds, and their most stable compounds are in this state. They have positive valences in compounds containing oxygen. The discussion in this chapter will be limited, for the most part, to compounds in which the halogens exhibit negative valence.

The Discovery of the Halogens. *Chlorine* was first prepared by Scheele in 1774 by the reaction of manganese dioxide with hydrochloric acid. *Iodine* was discovered by Courtois in 1811 in the form of a violet vapor produced by the reaction of hot concentrated sulfuric acid with a lye obtained from the ashes of seaweed. *Bromine* was prepared by Balard in 1826, as a product of the reaction of chlorine with certain marsh brines. Davy recognized the fact that compounds obtained from the mineral fluorspar contain an element similar to chlorine, and he named the element *fluorine,* even though

he was not able to isolate it. Fluorine was first prepared in 1886 by Moissan.

Occurrence of the Halogens. The activity of the halogens is so great that they are not found in the uncombined state among natural substances. They occur primarily in the form of binary salts, known as halides. *Chlorine*, the most abundant of the halogens, is estimated to account for only approximately 0.2 per cent of the matter in the outer part of the earth. Sodium chloride is the most abundant and important of the chlorides. This salt is the principal solid crystallized during the evaporation of sea water and salt lake waters. It is found in great salt deposits in different parts of the world, such as at Stassfurt in Germany and in similar deposits in a number of the states in the United States. This salt is the natural source of chlorine and its compounds and of sodium and the sodium compounds. *Bromides* also occur in sea water and in salt deposits. The per cent of combined bromine in sea water is only about 0.006. Bromine is produced from sea water and from salt well brines. *Iodides* likewise occur in sea water, but the percentage of the iodides is so small that salt brines usually are not a practical source of the element. The residues produced by charring certain varieties of marine plants contain small percentages of iodides. Salt brines, separated from certain oil wells in California and Louisiana, contain a high enough concentration of iodides to serve as a source of this halogen. *Sodium iodate*, $NaIO_3$, a salt of an oxyacid, is found in the sodium nitrate deposits in Chile. *Fluorides* do not occur associated with the other halides in salt deposits. The most important of the natural compounds of fluorine is *calcium fluoride*, CaF_2, a mineral known as fluorspar. The element also occurs in the mineral, *cryolite*, Na_3AlF_6.

Preparation of the Halogens. The halogens have a valence of $1-$ in their binary salts and acids. Free elements are in a zero valence state. The preparation of an elementary halogen, consequently, requires raising the valence from $1-$ to 0. *An increase in the valence of an element is called oxidation. The opposite change, a decrease in valence, is reduction.* The processes of oxidation and reduction occur simultaneously, and the relative numbers of atoms involved are such that the total number of units change in positive and negative valence are equal. Reactions in which atoms undergo changes in

valence are *oxidation-reduction reactions*. A more specific definition, in terms of the electronic changes, will be stated subsequently in Chapter 13. Substances that cause an increase in the valence of some other element are *oxidizing agents*, and those that cause a decrease are *reducing agents*. The fluorides are so stable toward oxidation that fluorine is not produced by the action of chemical oxidizing agents. Chlorine, bromine, and iodine are prepared by oxidation reactions. Potassium chlorate, potassium permanganate, and manganese dioxide are suitable oxidizing agents for use in the production of these elementary halogens from their binary compounds.

Laboratory Preparation of the Halogens. *Chlorine* is usually prepared in a laboratory process by oxidation of hydrochloric acid by manganese dioxide. The apparatus is shown in Fig. 55. Manganese dioxide is placed in the generator flask, and concentrated hydrochloric acid is added through the thistle tube. When the flask is heated gently, chlorine gas is evolved. It passes out through the delivery tube and is washed to remove hydrogen chloride gas, carried along mechanically, by bubbling it through a small volume of water. Chlorine is collected by the upward displacement of air in a bottle which is covered loosely. This method of collecting the gas is commonly used because chlorine is moderately soluble in water and is more dense than air. The products of the reaction are manganous chloride, water, and free chlorine.
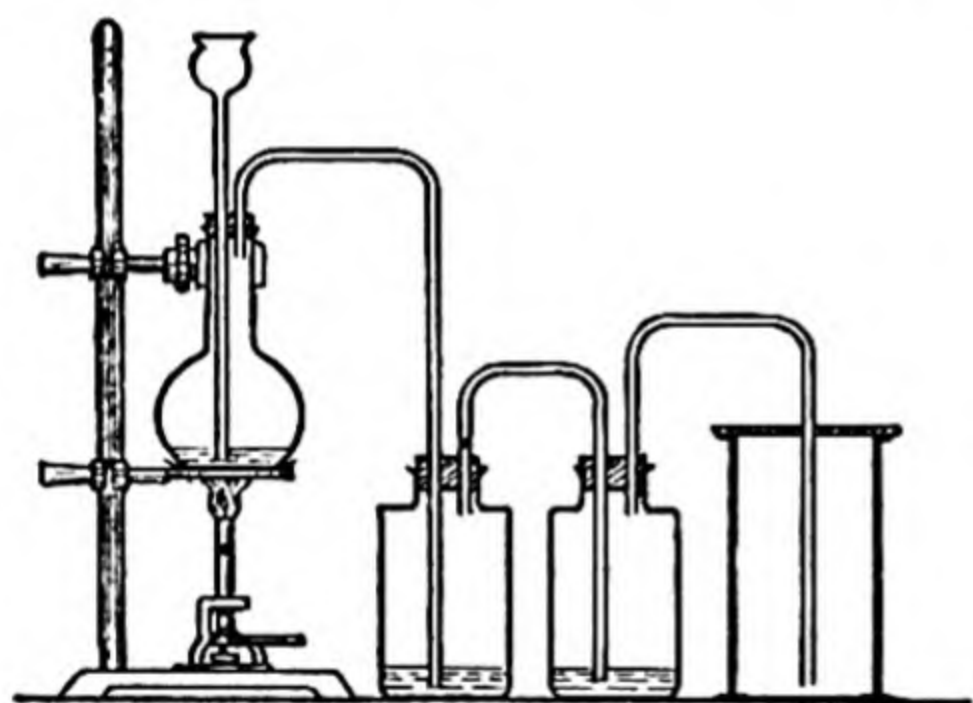
Fig. 55. *Laboratory Preparation of Chlorine*

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$$

Sodium chloride is sometimes used in preference to hydrochloric acid in the laboratory preparation of chlorine. An acid is required along with the manganese dioxide to produce chlorine from the salt. A mixture of manganese dioxide and salt is placed in the flask, and concentrated sulfuric acid is added through the thistle tube. The equation for the reaction is:

$$2\,NaCl + MnO_2 + 3\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + MnSO_4 + Cl_2 + 2\,H_2O$$
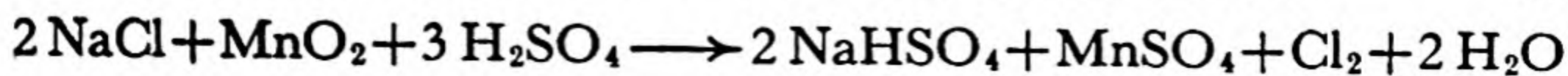
Bromine is evolved as a gas in a similar reaction, when a mixture of sodium bromide, manganese dioxide, and concentrated sulfuric acid is heated. The apparatus (Fig. 56) is arranged so that bromine does not come in contact with rubber stoppers or tubes, and the gas is condensed to liquid beneath water in a receiving tube.

$$2\,NaBr + MnO_2 + 3\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + MnSO_4 + Br_2 + 2\,H_2O$$
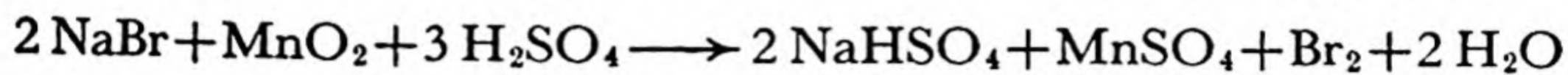
Similarly, *iodine* may be distilled from a mixture of sodium iodide, manganese dioxide, and concentrated sulfuric acid. The vapor condenses directly to the solid.

$$2\,NaI + MnO_2 + 3\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + MnSO_4 + I_2 + 2\,H_2O$$
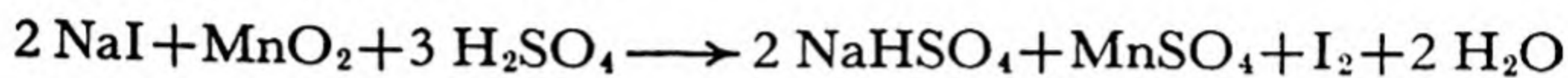
Industrial Preparation of the Halogens. *Chlorine* is prepared industrially by electrolysis of solutions of sodium chloride. This process — described in the preceding chapter, page 151, in connection with the production of sodium hydroxide — is the principal source of chlorine, although possibly 15 per cent of the total is obtained as a coproduct of processes operated primarily for other substances, *e.g.*, the electrolysis of fused sodium chloride for metallic sodium, of fused magnesium chloride for magnesium, and of potassium chloride solutions for potassium hydroxide.
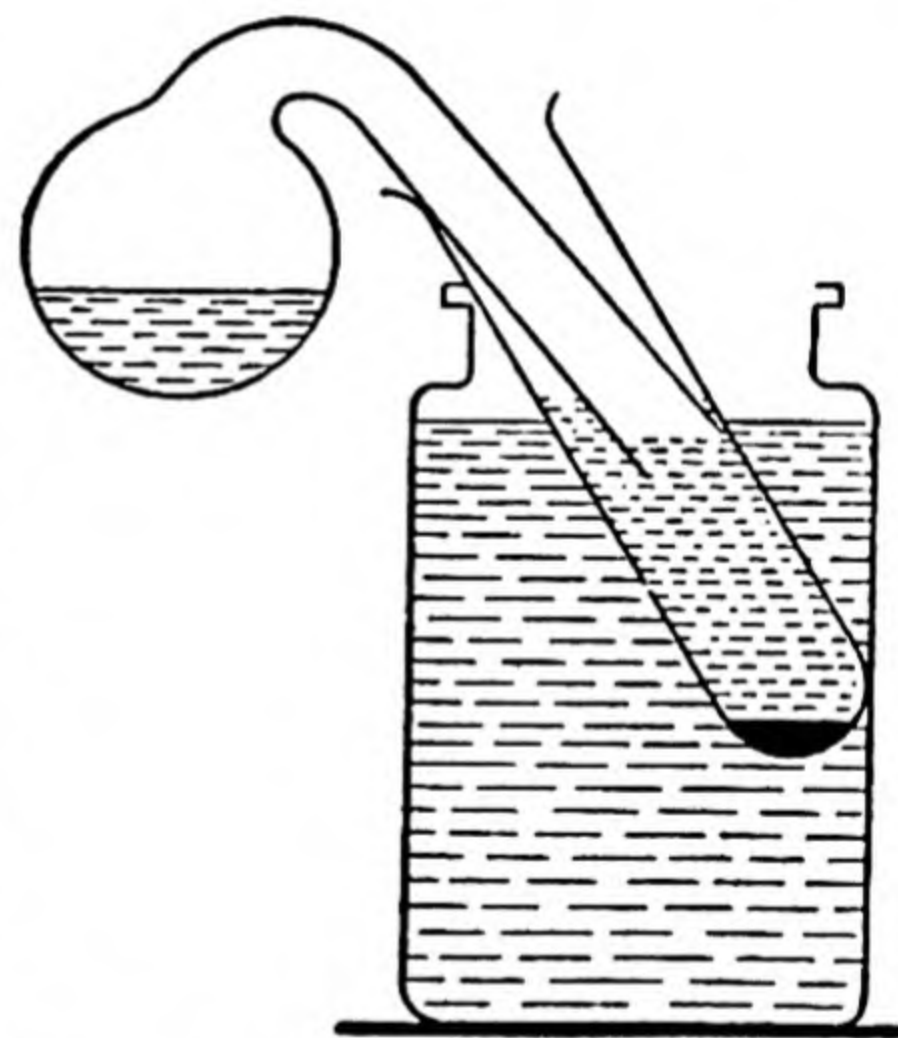
Fig. 56. *Laboratory Preparation of Bromine*

Bromine is obtained industrially in the United States from two main sources, *viz.*, salt well brines in Michigan and sea water at plants in North Carolina and on the Gulf coast in Texas. It is commonly produced by the action of chlorine on bromides.

$$Cl_2 + 2\,NaBr \longrightarrow Br_2 + 2\,NaCl$$
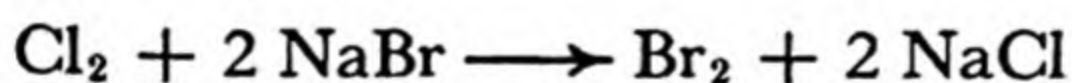
Bromine is evaporated by blowing warm air through the solution. Part of the vapor is condensed directly to liquid state, and the

remainder is absorbed in a solution of sodium carbonate to form the bromide and the bromate. Bromine is subsequently recovered from these salts.

Iodine is prepared industrially from iodides, by displacement with chlorine. An American process was developed in 1934 for the production of iodine from brines obtained from certain oil wells mentioned previously. Silver iodide is first precipitated by adding just enough of a dilute solution of silver nitrate to react with the iodides but not with the chlorides in the brine. This is possible because silver iodide is much less soluble than the chloride.

$$AgNO_3 + NaI \longrightarrow AgI \downarrow + NaNO_3$$
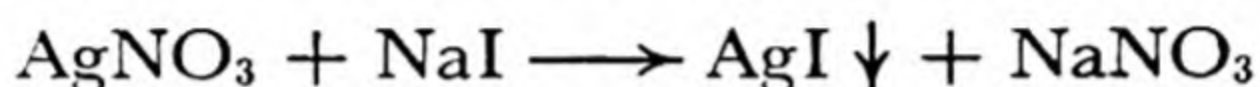
Clean steel scrap is next added to a suspension of the iodide, which has been separated from the brine. Iron displaces silver, forming ferrous iodide.

$$2\,AgI + Fe \longrightarrow FeI_2 + 2\,Ag$$
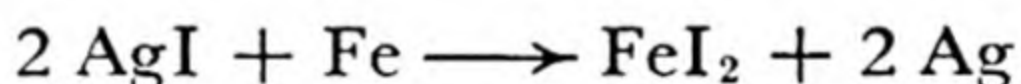
Silver is separated and converted into the nitrate for repeated use. Iodine is now displaced from ferrous iodide by the action of chlorine.

$$FeI_2 + Cl_2 \longrightarrow FeCl_2 + I_2$$
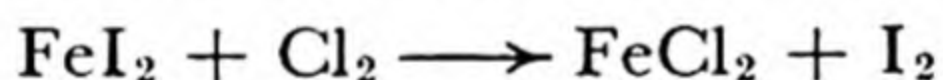
Iodine is also prepared from sodium iodate, $NaIO_3$. The valence of iodine in this compound is $5+$, so that a process of reduction is required for the production of the free element. An acid is also necessary, and sodium hydrogen sulfite serves as both the reducing agent and the acid.

$$2\,NaIO_3 + 5\,NaHSO_3 \longrightarrow I_2 + 2\,Na_2SO_4 + 3\,NaHSO_4 + H_2O$$
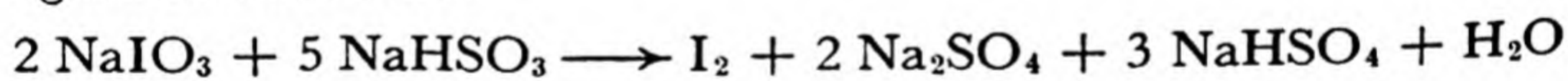
Fluorine is now prepared by the electrolysis of fused potassium hydrogen fluoride, KHF_2, in a copper vessel. The inner surface of the cell becomes coated with a thin film of copper fluoride, which adheres to the surface, and protects it from further corrosion by fluorine.

Properties of the Halogens. Some of the properties of these elements are listed in Table 12.

A gradation in properties from fluorine to iodine is observed when the elements are arranged in the order of their atomic weights. The density, melting point, boiling point, and critical temperature all increase from element to element in this order. There is also

an increase in the depth of color in the gaseous state: fluorine, pale yellow; chlorine, greenish-yellow; bromine, reddish-brown; and

TABLE 12. PROPERTIES OF THE HALOGENS

Property	Fluorine	Chlorine	Bromine	Iodine
Atomic weight	19.00	35.46	79.92	126.92
Molecular weight	38.00	70.92	159.84	253.84
State at 20°	Gas	Gas	Liquid	Solid
Melting point (° C.)	− 223.0	− 102.0	−7.3	114.0
Boiling point (° C.)	− 187.0	− 33.7	58.8	183.0
Critical temp. (° C.)	——	144.0	302.0	553.0

iodine, violet. The solubility of chlorine in water, at 20° and a pressure of one atmosphere of the gas, is 0.64 g. in 100 g. of water; bromine, 3.2 g., in 100 g. of water; and iodine, 0.034 g. in 100 g. of water. Fluorine reacts with water. The halogens are less soluble in water than in alcohol, carbon tetrachloride, or some other organic solvents. Iodine dissolves readily in solutions of potassium iodide. In the gaseous state at moderate temperatures, the halogens exist as diatomic molecules. The molecules decompose into the individual atoms at high temperatures. Mixtures of diatomic and monatomic molecules are obtained at intermediate temperatures.

In the gaseous state, the halogens have disagreeable odors and an irritating effect on the mucous membrane lining the nose and throat. The use of chlorine as a military gas during the great war of 1914–1918 was an application of this property. The action of fluorine is more severe, though much less familiar, than that of chlorine. Liquid bromine produces severe burns if it comes in contact with the skin, and great care should be exercised to avoid spilling. At room temperature, iodine has no severe corrosive action on the skin.

Reactions of the Halogens. These four nonmetals exhibit reactions of the same variety but of different intensity. Chlorine serves as a type to illustrate the reactions of the group.

Reactions of Chlorine. Chlorine reacts vigorously with most of the other elements. The union of chlorine with the metallic elements leads to the formation of binary salts, chlorides. *Chlorine unites with all of the familiar metals,* reacting slowly with the inactive metals gold and platinum. The reaction with the more active

metals takes place so rapidly that the metals burn in an atmosphere of this gas.

$$Cu + Cl_2 \longrightarrow CuCl_2$$
$$2\,Sb + 3\,Cl_2 \longrightarrow 2\,SbCl_3$$
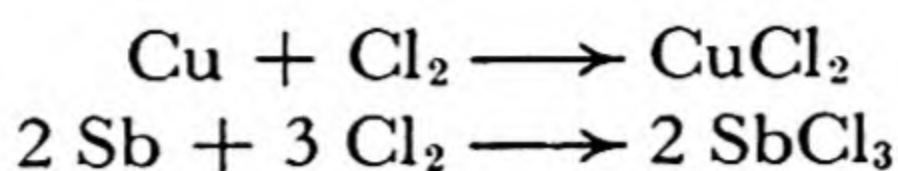
A trace of moisture is required for this reaction, and therefore dry chlorine may be stored in steel cylinders without attacking the metal.

Chlorine reacts also with most of the nonmetals but this is less vigorous than the reactions with many of the active metals. Phosphorus, however, burns in an atmosphere of the gas, forming first the trichloride which combines with additional chlorine to form the pentachloride.

$$2\,P + 3\,Cl_2 \longrightarrow 2\,PCl_3$$
$$PCl_3 + Cl_2 \longrightarrow PCl_5$$
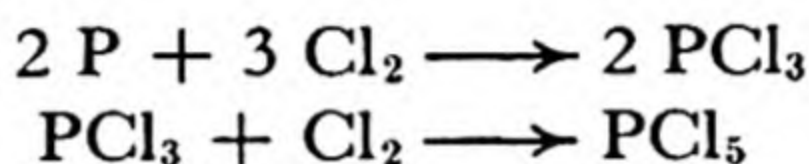
Carbon, oxygen, and nitrogen do not unite directly with chlorine, but chlorides of these elements can be formed by other methods.

Hydrogen burns in an atmosphere of chlorine if a trace of moisture is present. Mixtures of moist chlorine and hydrogen are stable in the dark, but react with explosive violence when exposed to light rich in rays of short wave length. Energy absorbed from the light activates the atoms of the halogens sufficiently to start the reaction. The combination of hydrogen and chlorine is highly exothermic.

$$H_2 + Cl_2 \longrightarrow 2\,HCl + 44,600 \text{ cal.}$$
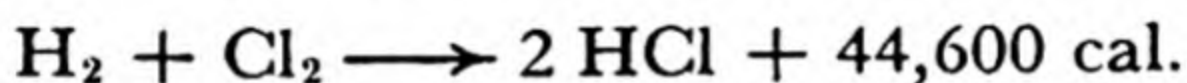
Chlorine reacts with many of the hydrocarbons, the binary compounds of carbon with hydrogen. Two types of reaction of chlorine with hydrocarbons may occur. One type is known as a *substitution reaction,* because atoms of chlorine are substituted for atoms of hydrogen. This is not a simple replacement, as in the reaction of metals with acids, since the hydrogen removed from the molecule combines with chlorine to form hydrogen chloride. Reacting with methane, CH_4, methyl chloride, CH_3Cl, is formed as the first product of substitution.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
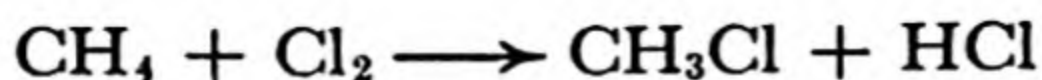
Substitution of other atoms of hydrogen may continue, producing carbon tetrachloride, CCl_4, as the final product. The other type

of reaction of a halogen with a hydrocarbon is an *addition reaction.* Molecules of certain classes of hydrocarbons may add pairs of halogen atoms to form more complex products. Thus, ethylene, C_2H_4, adds chlorine to form ethylene dichloride.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$
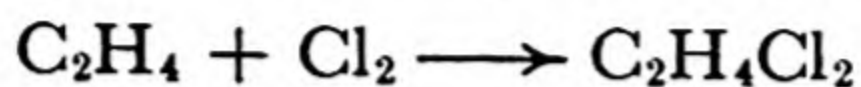
Chlorine reacts with water, yielding a mixture of hydrochloric acid and hypochlorous acid. The reaction is reversible, and an equilibrium mixture is produced.

$$H_2O + Cl_2 \rightleftharpoons HCl + HClO$$
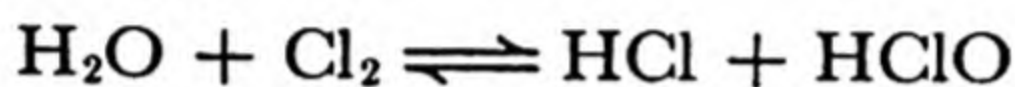
Hypochlorous acid is unstable in direct sunlight, decomposing slowly to form hydrochloric acid and oxygen.

$$2\ HClO \longrightarrow 2\ HCl + O_2$$
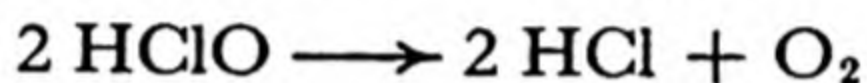
The decomposition of hypochlorous acid prevents equilibrium in this system, and the reaction of water with chlorine becomes completed in sunlight.

Chlorine reacts with solutions of basic hydroxides. In cold solution, a mixture of chloride and hypochlorite in equimolar quantities is produced.

$$2\ KOH + Cl_2 \longrightarrow KCl + KClO + H_2O$$

The hypochlorite is converted into a mixture of chloride and chlorate in hot solution.

$$3\ KClO \longrightarrow 2\ KCl + KClO_3$$
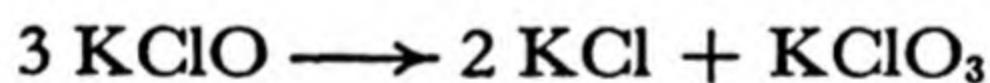
Chlorine displaces a number of other nonmetals from their binary compounds. The preparation of bromine and iodine by the reaction of their salts with chlorine is based on this property. Chlorine also reacts with sulfides, displacing sulfur.

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$
$$H_2S + Cl_2 \longrightarrow 2\ HCl + S$$
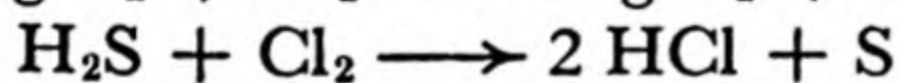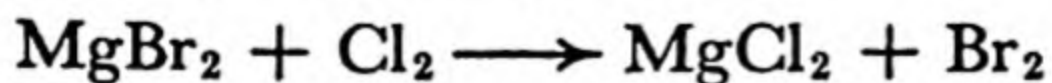
Relative Activities of the Halogens. The four halogens enter into reactions of the types illustrated by chlorine. The differences in their behavior are due to differences in activity. Mixtures of moist hydrogen and fluorine react violently, even when they are cold and are protected from light. Mixtures of moist hydrogen and chlorine do not react when they are cold and are shielded from

light, but react explosively when exposed to ultraviolet light. Hydrogen and bromine do not react readily unless they are heated or passed in contact with a catalyst such as platinum. The reaction of hydrogen and iodine is slow and incomplete, even when the gases are heated together and are in the presence of a catalyst. The heats of reaction of the halogens with hydrogen show the order of their activities. The number of calories in the formation of 2 moles of the hydride is shown in the equation.

$$H_2 + F_2 \longrightarrow 2\ HF + 127{,}980\ cal.$$
$$H_2 + Cl_2 \longrightarrow 2\ HCl + 44{,}600\ cal.$$
$$H_2 + Br_2 \longrightarrow 2\ HBr + 17{,}300\ cal.$$
$$H_2 + I_2 \rightleftharpoons 2\ HI - 11{,}850\ cal.$$
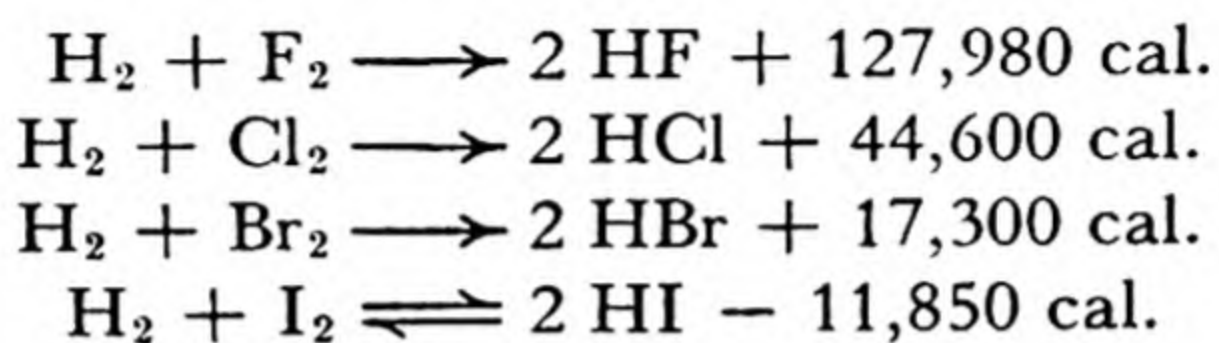
The relative activities of the halogens are shown also by their displacement reactions. Fluorine, chlorine, and bromine displace iodine from its binary salts, but iodine displaces none of the other members of the family. Similarly, fluorine and chlorine displace bromine, and fluorine displaces chlorine. When the halogens are arranged in the order of their atomic weights, it is observed that each is less active than those preceding it in the list. This order of activity is directly opposite to that observed among the alkali metals.

Tests for the Elementary Halogens. The presence of a free halogen in considerable concentration may be recognized by color, odor, and other simple physical properties. A dark blue product is formed when iodine is added to a suspension of finely divided starch in water. This test reaction is not shown by iodine compounds. Since bromine and chlorine displace iodine from iodides, the starch test is sometimes used indirectly for the presence of these elements. But this is not a conclusive test, since there are a number of other substances that liberate iodine from iodides. A delicate test is based on the high solubility of bromine and iodine in solvents such as chloroform, carbon tetrachloride, and carbon disulfide, and on the characteristic color exhibited by such solutions containing the halogen. If a solution containing small concentrations of bromine or iodine is extracted with one of these solvents, the halogen is concentrated in the nonaqueous layer. Iodine gives a characteristic purple color and bromine a red color in these solvents.

Industrial Uses of the Halogens. *Chlorine* is industrially the most important of the halogens. It is estimated * that the production of chlorine in 1943 in the United States was approximately 1,200,000 tons — a great increase compared to 1942. The most extensive uses of chlorine are now in the chemical industries. It is employed not only in the direct formation of important compounds such as hypochlorites but particularly in the organic chemical industry in preparing materials which are intermediates in the formation of other substances.

Chlorine is used extensively as a bleaching agent. The bleaching action of chlorine is due to the formation of hypochlorous acid in the presence of water.

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$
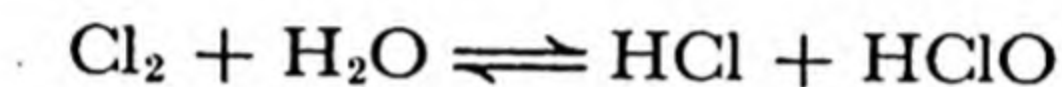
There are a number of colored substances, in natural fibers, that are changed to colorless products by reaction with oxygen. Many of these substances are not affected by atmospheric oxygen, but are bleached by hypochlorous acid, which has a more vigorous oxidizing action. Wood pulp, linen, and cotton are composed chiefly of cellulose, with such low chemical activity that it is affected only slowly by dilute solutions of hypochlorous acid. The coloring substances are more active and are oxidized. After the bleaching is complete, the excess of chlorine and hypochlorous acid must be removed to prevent damage to the fabric. This is done by washing with water and by the use of chemical substances, such as sodium thiosulfate, $Na_2S_2O_3$. Wool and silk are composed largely of proteins, which are more active than cellulose toward chlorine and hypochlorous acid. Consequently, they cannot be bleached by chlorine without injury.

The use of chlorine as a disinfecting and deodorizing agent is also dependent on the formation of hypochlorous acid. Among important uses of chlorine in sanitation are the treatment of public water supplies and of sewage, and the preparation of germicidal solutions.

During the world war of 1914–1918, chlorine was extensively used in the production of poison gases for military use. The first extensive use of poison gas as an offensive weapon was made by

* *Chem. Met. Eng.* **51,** 119 (1944).

the German army at Ypres in Belgium, in the spring of 1915. Elementary chlorine was liberated from cylinders on a day when the wind direction and velocity were suitable to cause a great cloud of the gas to sweep down over and into the trenches of the Allies. Later, more effective compounds were developed for military use. The most important of those used during that war is mustard gas, $(C_2H_4Cl)_2S$, a liquid substance suitable for use in shells. The explosion of the shell scatters the liquid over a large area where it persists for some time. The evaporation of this liquid produces a dense vapor which acts as both a skin and a lung irritant. Lewisite, $C_2H_2ClAsCl_2$, developed by the American chemist W. Lee Lewis too late for use during the preceding world war, is still more effective. It is an oily liquid of relatively high boiling point. It produces a dense gas acting as a sternutator, a substance which causes sneezing and thus may prevent the effective use of a gas mask; a lachrymator, a tear gas with a blinding effect; a vesicant, a substance producing skin blisters; and a lung irritant. It also causes arsenic poisoning.

Bromine is important in the production of a number of compounds, such as potassium bromide used medicinally as a sedative, and silver bromide used as a light-sensitive salt in photography. A number of bromine compounds are important as intermediates in the synthesis of organic chemicals. The most extensive use of bromine is in the production of ethylene dibromide, $C_2H_4Br_2$, which is employed in small proportions in the preparation of ethyl gasoline. Ethyl gasoline contains tetraethyl lead as an "antiknock." The combustion of this material in an internal combustion engine produces a deposit of lead oxide, which is harmful. Ethylene dibromide furnishes bromine to combine with lead, forming the bromide which is discharged with the exhaust gases.

Iodine is used directly in the familiar tincture of iodine, a solution of the element in alcohol. The tincture may contain enough potassium iodide to permit dilution with water without precipitating iodine. A number of iodine compounds are prepared from the element. Some of these have important applications in medicine and in photography.

Fluorine has few direct uses of importance, although several of its compounds are important. One of the important compounds

is the methane substitution product, difluorodichloromethane, CF_2Cl_2, which may be prepared by the interaction of carbon tetrachloride and antimony trichloride in the presence of antimony pentafluoride. Under the trade name Freon, it is used in some household refrigerating machines. In addition to suitable boiling and freezing points, it has the advantage of being nontoxic and noninflammable in the event that leaks develop in the refrigerating system.

THE HYDROHALIC ACIDS

The hydrides of the halogens are highly soluble in water, and the aqueous solutions show to a high degree the general reactions characteristic of acids. These binary acids are the hydrohalic acids. There are also a few additional nonmetal hydrides that have acidic properties. None of the hydrohalic acids occurs among natural substances in industrially important proportions. Hydrochloric acid is the most important of these substances. Gaseous hydrogen chloride is a component of some volcanic gases, and a small percentage of the substance is present as an important component of the gastric juices.

Preparation of the Hydrohalic Acids. These substances are usually produced by first preparing the gaseous hydrogen halides, which are then absorbed in water. Four reactions are available for the production of the hydrogen halides, *viz.*, double decomposition between an acid of high boiling point and a salt of the hydroacid; direct union of hydrogen and the halogen; displacement of less active nonmetals from their hydrides by the halogens; and the reaction of certain nonmetal halides with water.

Hydrogen chloride and hydrogen fluoride are usually prepared by heating a mixture of concentrated sulfuric acid and the appropriate salt. The hydrogen halides are so soluble in water that the reaction does not occur when dilute solutions of the acid and the salt are mixed. The hydrogen halides are not soluble in concentrated sulfuric acid and the evaporation of the gases causes the completion of the reaction. The reaction of sodium chloride with concentrated sulfuric acid occurs in two stages. The first reaction takes place at moderate temperatures, producing the hydrosulfate, $NaHSO_4$, and hydrogen chloride.

$$NaCl + H_2SO_4 \longrightarrow HCl \uparrow + NaHSO_4$$
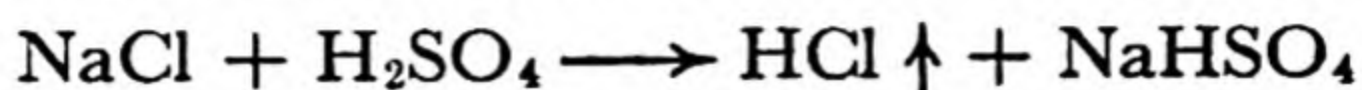
At a temperature of about 500°, the second stage of the reaction occurs.

$$NaCl + NaHSO_4 \longrightarrow HCl \uparrow + Na_2SO_4$$

In the laboratory preparation, the gas may be collected by the upward displacement of air in an upright jar, as in the collection of chlorine. Industrially, it is absorbed in water, forming hydrochloric acid solution.

Hydrofluoric acid attacks glass, so that the reaction of calcium fluoride and concentrated sulfuric acid is carried out by warming the materials in a retort made of platinum or of lead.

$$CaF_2 + H_2SO_4 \longrightarrow 2\,HF \uparrow + CaSO_4$$
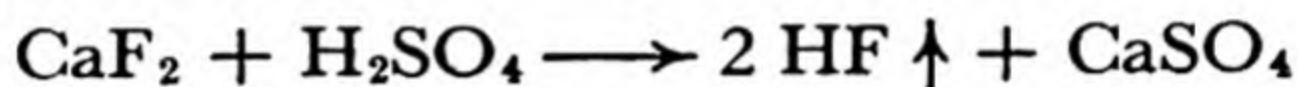
The product may be condensed to a liquid with a boiling point of 20° or may be absorbed in water.

The hydrides of bromine and iodine are less stable toward oxidation than the hydrides of fluorine and chlorine, because the elements are less active. Hot concentrated sulfuric acid is active enough as an oxidizing agent to convert hydrogen bromide and hydrogen iodide more or less completely into the free halogens and water. The reduction product of sulfuric acid is sulfur dioxide with the bromide and hydrogen sulfide with the iodide.

$$2\,HBr + H_2SO_4 \longrightarrow 2\,H_2O + Br_2 + SO_2$$
$$8\,HI + H_2SO_4 \longrightarrow 4\,H_2O + 4\,I_2 + H_2S$$
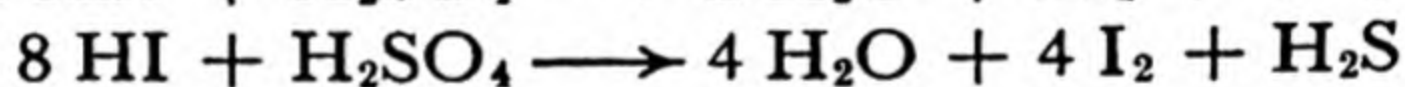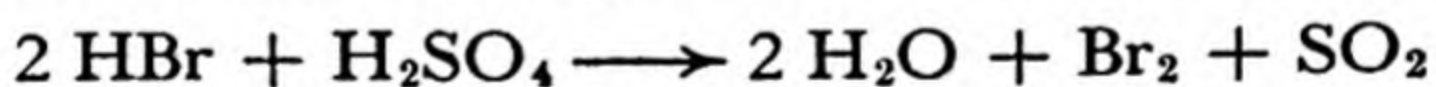
The reaction of bromides and iodides with phosphoric acid may be used for the laboratory preparation of hydrogen bromide and hydrogen iodide, respectively, but is not used industrially. Phosphoric acid has a suitably high boiling point and lower oxidizing activity than sulfuric acid.

$$NaBr + H_3PO_4 \longrightarrow HBr \uparrow + NaH_2PO_4$$
$$KI + H_3PO_4 \longrightarrow HI \uparrow + KH_2PO_4$$
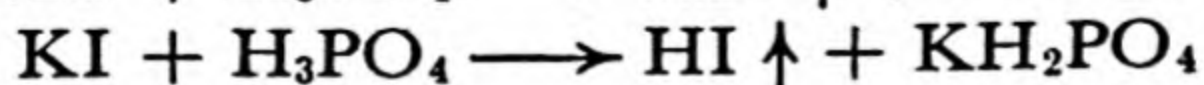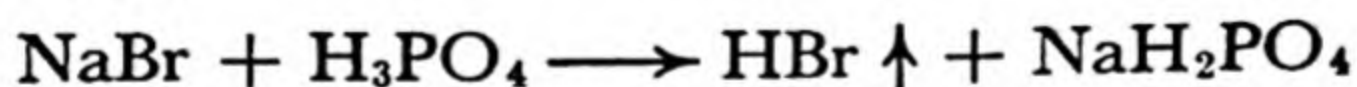
Hydrogen bromide and hydrogen iodide are commonly prepared by the direct union of the elements. Hydrogen chloride is sometimes prepared by this reaction also, but the method is not economically practicable unless large quantities of chlorine are available at low cost, as in the electrolytic production of magnesium from its chlo-

ride. The reaction of hydrogen with bromine is catalyzed by porous charcoal and by platinum gauze to give a suitable rate of reaction at 200°. The reaction of hydrogen with iodine takes place in the presence of a heated catalyst, but — since the reaction is reversible — an equilibrium mixture is formed. In industrial practice, the reaction is carried out with the gases at a pressure of 200 lb. per square inch at a temperature of 150–200°, with chromic acid as a catalyst, and with the gases enclosed over water. Hydrogen iodide dissolves in water, thus displacing the equilibrium and increasing the yield.

Solutions of hydriodic acid are conveniently prepared by passing hydrogen sulfide into a suspension of pulverized iodine. Sulfur is displaced, leaving hydriodic acid in solution.

$$H_2S + I_2 \longrightarrow 2\,HI + S$$
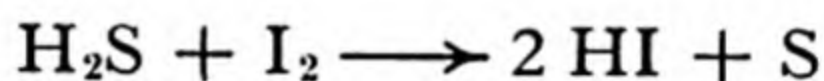
This reaction is not important for the production of the other hydrohalic acids.

Several of the nonmetal halides, such as the trihalides of phosphorus, react with water to form hydrogen halide and phosphorous acid. This reaction is of limited importance. In the preparation of hydrobromic acid by this method, the reaction of bromine with phosphorus and of tribromide with water occur in a single step. Bromine is allowed to drop into a suspension of red phosphorus in a small quantity of water. (Fig. 57.) The reacting mixture gets so hot that some bromine vapor is carried along with the hydrogen

Fig. 57. Laboratory Preparation of Hydrobromic Acid

bromide. This may be removed by passing the gas through a tube containing glass beads coated with moist red phosphorus.

$$2\,P + 3\,Br_2 \longrightarrow 2\,PBr_3$$
$$PBr_3 + 3\,H_2O \longrightarrow 3\,HBr \uparrow + H_3PO_3$$
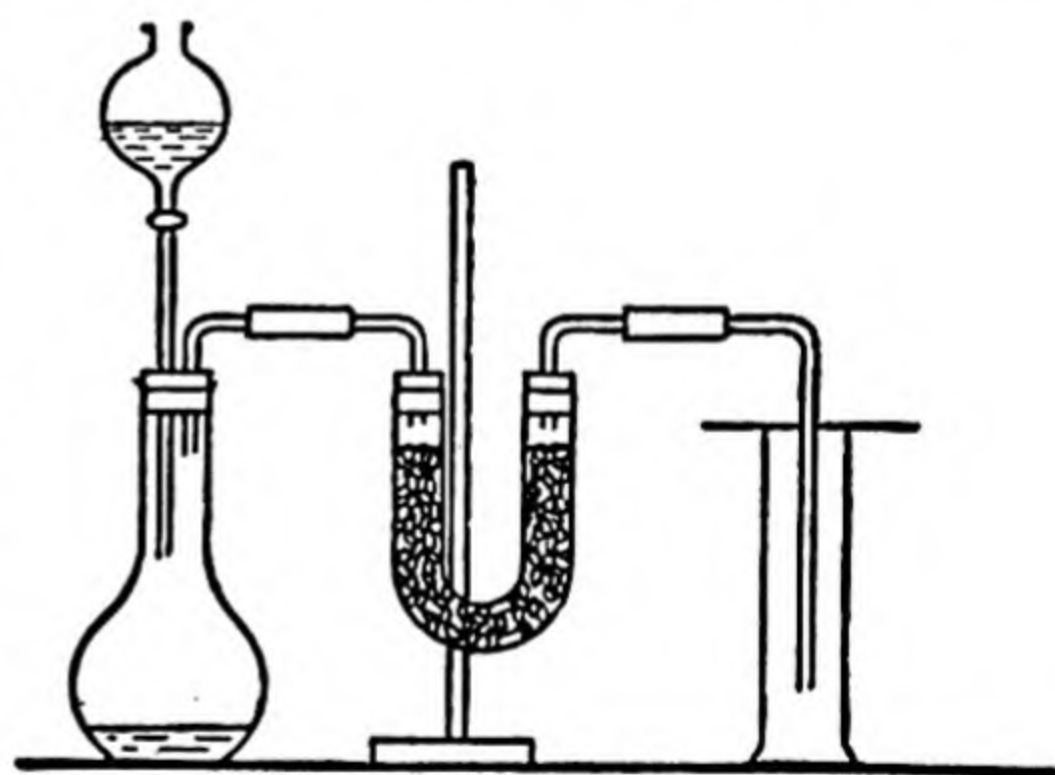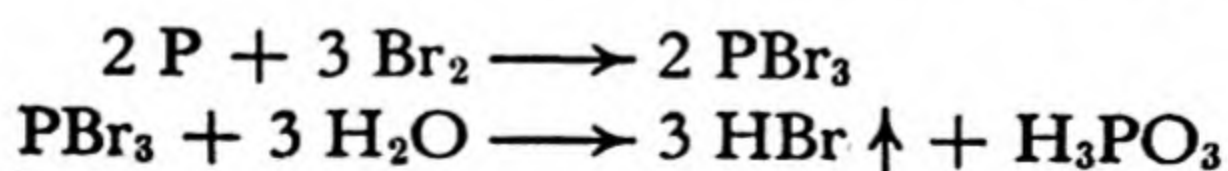
Phosphorous acid remains dissolved in the water in the flask.

Properties of the Hydrogen Halides. These substances are colorless gases at room temperature, with the exception of hydrogen fluoride which has a boiling point of 20°. They are highly soluble in water, and the gases fume in moist air because the condensation of water vapor forms a fog of minute droplets of the acidic solution. The gases have disagreeable odors and irritate the lining of the nose and throat. In the liquid state they are poor conductors of electricity, but aqueous solutions are good conductors. Molecular weight determinations show that the gaseous molecules are composed of one atom each of hydrogen and the halogen, with the exception of hydrogen fluoride at low temperatures. At temperatures below 100°, hydrogen fluoride is partly in the form of complex molecules, H_6F_6, about 80 per cent at 20°. The molecular form, such as H_6F_6, is a polymer of the simple molecule, HF. *A polymer has the same composition as the simpler form, but its molecular weight is an integral multiple of the simple formula weight.* Each of the hydrogen halides forms a constant boiling solution with water. Some of the properties of these substances are tabulated in Table 13.

TABLE 13. PROPERTIES OF THE HYDROGEN HALIDES

Property	HF	HCl	HBr	HI
Boiling point (° C.)	20	− 85	− 67	− 36
Melting point (° C.)	− 83	− 114	− 87	− 51
Critical temperature (° C.)	—	51.4	90.0	151.0
Constant boiling solution				
a. Boiling point (° C.)	120	110	126	127
b. Per cent of weight of acid	35.4	20.24	47	57

Reactions of the Hydrohalic Acids. Each of these acids exhibits two series of reactions, *viz.*, the general acid reactions and reactions due to the simple halide radicals. The hydrohalic acids resemble each other closely, not only because they have in common the properties of acids, but also because the reactions due to the halide radicals are similar.

The typical acid reactions of the hydrohalic acids are those with active metals, metal oxides, metal hydroxides, ammonia, and with salts of acids that are less active, less soluble, or unstable at room temperature. Some of these reactions are reversible to some extent, but are practically complete in the presence of an excess of the acid. The following equations represent typical acid reactions of

hydrochloric acid, and a similar series of equations may be written for each of the other hydrohalic acids.

$$Mg + 2\,HCl \longrightarrow H_2 + MgCl_2$$
$$ZnO + 2\,HCl \longrightarrow H_2O + ZnCl_2$$
$$Ca(OH)_2 + 2\,HCl \longrightarrow 2\,H_2O + CaCl_2$$
$$NH_3 + HCl \longrightarrow NH_4Cl$$
$$CaCO_3 + 2\,HCl \longrightarrow H_2O + CO_2 \uparrow + CaCl_2$$
$$FeS + 2\,HCl \longrightarrow H_2S \uparrow + FeCl_2$$
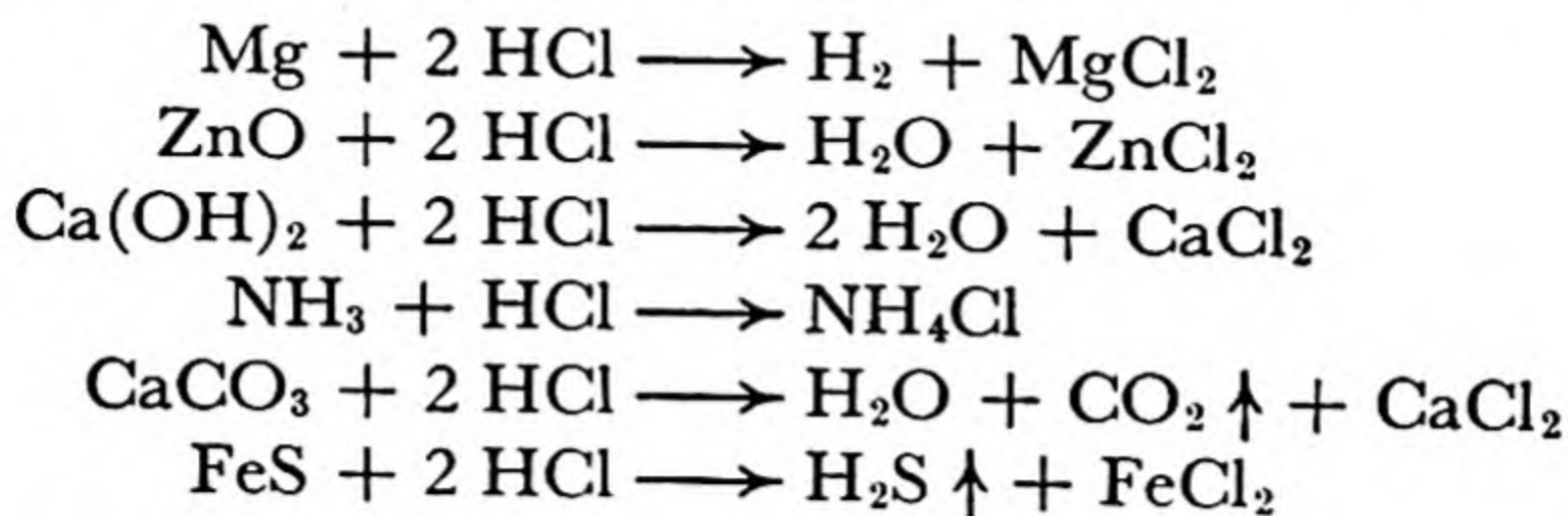
Due to their halide radicals, the hydrohalic acids react with the soluble salts of metals, yielding precipitates of slightly soluble halides. *Silver, lead, mercurous chlorides, bromides, iodides, and mercuric iodide are slightly soluble in water.* The other common salts of these acids are at least moderately soluble. Most of the fluorides have low solubility in water, but potassium and silver fluorides are highly soluble. Examples of precipitation reactions of these acids are shown by the equations:

$$AgNO_3 + HCl \longrightarrow AgCl \downarrow + HNO_3$$
$$Pb(NO_3)_2 + 2\,HBr \longrightarrow PbBr_2 \downarrow + 2\,HNO_3$$
$$Hg_2SO_4 + 2\,HI \longrightarrow Hg_2I_2 \downarrow + H_2SO_4$$
$$HgSO_4 + 2\,HI \longrightarrow HgI_2 \downarrow + H_2SO_4$$
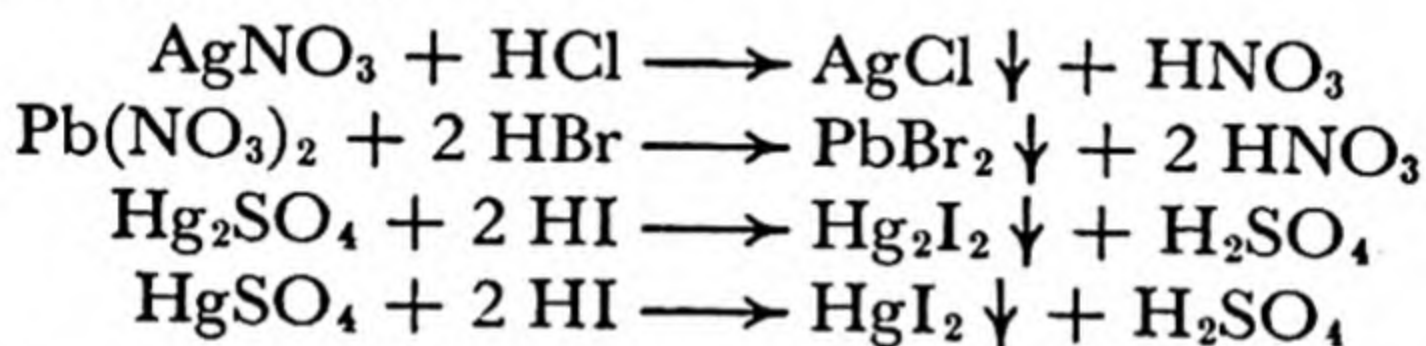
A second series of reactions of the hydrohalic acids, also due to the halide radicals, is *the reaction with suitable oxidizing agents to form the free halogens.* Hydrofluoric acid is so stable toward oxidation that it is not oxidized by any chemical agent. Hydrochloric, hydrobromic, and hydriodic acids are oxidized by manganese dioxide.

$$4\,HBr + MnO_2 \longrightarrow MnBr_2 + 2\,H_2O + Br_2$$
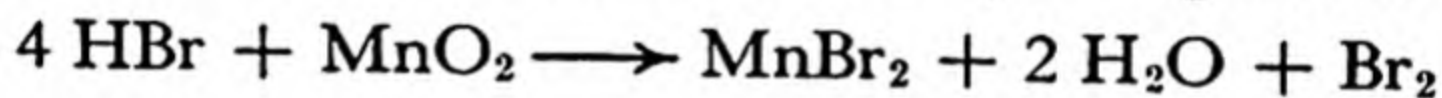
The most important reaction of hydrofluoric acid is with silica and silicates to form gaseous silicon tetrafluoride. This reaction is specific for hydrofluoric acid and is due to the great stability of silicon tetrafluoride. Common glass is composed of the silicates of sodium and calcium together with an excess of silicon dioxide. The reaction of these substances with hydrofluoric acid causes the etching of glass.

$$Na_2SiO_3 + 6\,HF \longrightarrow 2\,NaF + SiF_4 + 3\,H_2O$$
$$CaSiO_3 + 6\,HF \longrightarrow CaF_2 + SiF_4 + 3\,H_2O$$
$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O$$
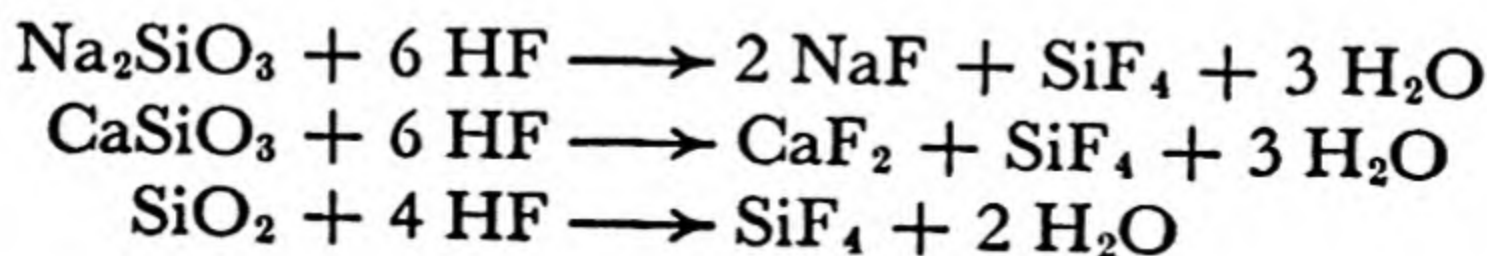
Markings on thermometer stems and on graduated flasks and cylinders are etched by coating the glass with paraffin and cutting through this coating to uncover the glass at the desired points. The unprotected areas of the glass are attacked when exposed to the acid.

Stability of the Hydrides of the Halogens. The most important differences in the behavior of the hydrohalic acids are due to differences in stability toward oxidizing agents. In the discussion of the activity of the halogens, it was shown that the amount of heat evolved in the formation of one mole of each of these hydrides is greatest for hydrogen fluoride and least for hydrogen iodide. Consequently, hydrogen fluoride is the most stable of these hydrides, and hydrogen iodide is the least stable. Neither hydrofluoric acid nor hydrochloric acid is oxidized by hot concentrated sulfuric acid, but hydrochloric acid is oxidized by manganese dioxide, whereas hydrofluoric acid is not. Both hydrobromic and hydriodic acids are oxidized by hot concentrated sulfuric acid and also by manganese dioxide, but hydriodic acid is oxidized by atmospheric oxygen, whereas hydrobromic acid is not.

Uses of the Hydrohalic Acids. Hydrochloric acid is the only one of this group of hydroacids which has extensive uses, because of its general acid reactions. It is used in the laboratory as a convenient active acid and also as a source of the chloride radical and of free chlorine. Commercially, it is used in the preparation of ammonium chloride for the manufacture of dry cells; for dissolving mineral matter from bone ash in the production of boneblack; in clarifying sugar solutions; in cleaning the rust from the surface of metals to be enameled; in the preparation of chlorides of metals; and in the manufacture of glue, dyes, soap, textiles, and many other products.

The uses of hydrofluoric acid are due to its reaction with silica and silicates. In addition to its use in the etching of glass, it is used in cleaning metal castings, polishing cut glass, and in the decomposition of complex silicates for analysis.

EXERCISES

1. Compare the members of the halogen group with reference to the following: (*a*) occurrence; (*b*) laboratory preparation; (*c*) industrial preparation; (*d*) properties; (*e*) varieties of reactions; (*f*) activity.

2. What general type of reaction is required for the production of halogens from halides?

3. Describe the common laboratory method for the preparation of chlorine.

4. Describe industrial methods for the preparation of (a) chlorine, (b) bromine, (c) iodine.

5. Represent by equations the reactions of the halogens with (a) metals, (b) non-metals, (c) hydrogen, (d) water, (e) hydroxides of metals, (f) salts of less active nonmetals.

6. Write equations for two series of reactions which show the relative activities of the members of the halogen group, and explain how these reactions show the order of activity.

7. Discuss the industrial importance of chlorine.

8. What two general methods are employed for the production of the hydrohalic acids? Which acids are commonly prepared by each of these methods?

9. Why is the reaction of concentrated sulfuric acid with a bromide or an iodide not suitable for the production of the corresponding hydrohalic acid? Why is reaction with dilute sulfuric acid not suitable?

10. Write equations to represent four different types of reactions shown by each of the hydrohalic acids. To which component of the acid are these reactions due?

11. Write equations to represent two specific reactions of each of the hydrohalic acids.

12. How does the stability of a hydrohalic acid indicate the activity of the halogen?

SUPPLEMENTARY READINGS

Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940, chap. VII.

Weeks, M. E., *The Discovery of the Elements*, Journal of Chemical Education, Easton, Pa., 1935, pp. 253–74.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 3–5.

Furnas, C. C., *Rogers Manual of Industrial Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, pp. 438–50.

Badger, W. L., and E. M. Baker, *Inorganic Chemical Technology*, McGraw-Hill Book Company, Inc., New York, 1941, chap. V.

Stewart, L. C., "Bromine from Sea Water," *Ind. Eng. Chem.* **26**, 361 (1934).

Robertson, G. R., "New American Iodine Industry," *Ind. Eng. Chem.* **26**, 374 (1934).

Mantell, C. L., "Modern Chlorine Practice," *Chem. Met. Eng.* **47**, 396 (1940).

"Bromine from Sea Water," Pictured Flow Sheet, *Chem. Met. Eng.* **46**, 12, 771 (1939).

"Electrolytic Chlorine and Caustic Soda," Pictured Flow Sheet, *Chem. Met. Eng.* **49**, 12, 114 (1942).

Chapter 12

THE PERIODIC SYSTEM

Dalton's atomic theory emphasizes the atomic weight as the distinguishing feature of an element. Two related groups of elements have now been discussed in some detail, and variations in the properties and the reactions of the elements within a group have been associated with differences in atomic weights. In this chapter, a system including all elements is discussed, and some of its applications in later sections are indicated.

The Periodic System of Mendeléef. The fundamental principle employed in the classification of the elements was stated by Mendeléef in 1869 as the **Periodic Law: The properties of the chemical elements are periodic functions of their atomic weights.** The same principle was recognized about the same time
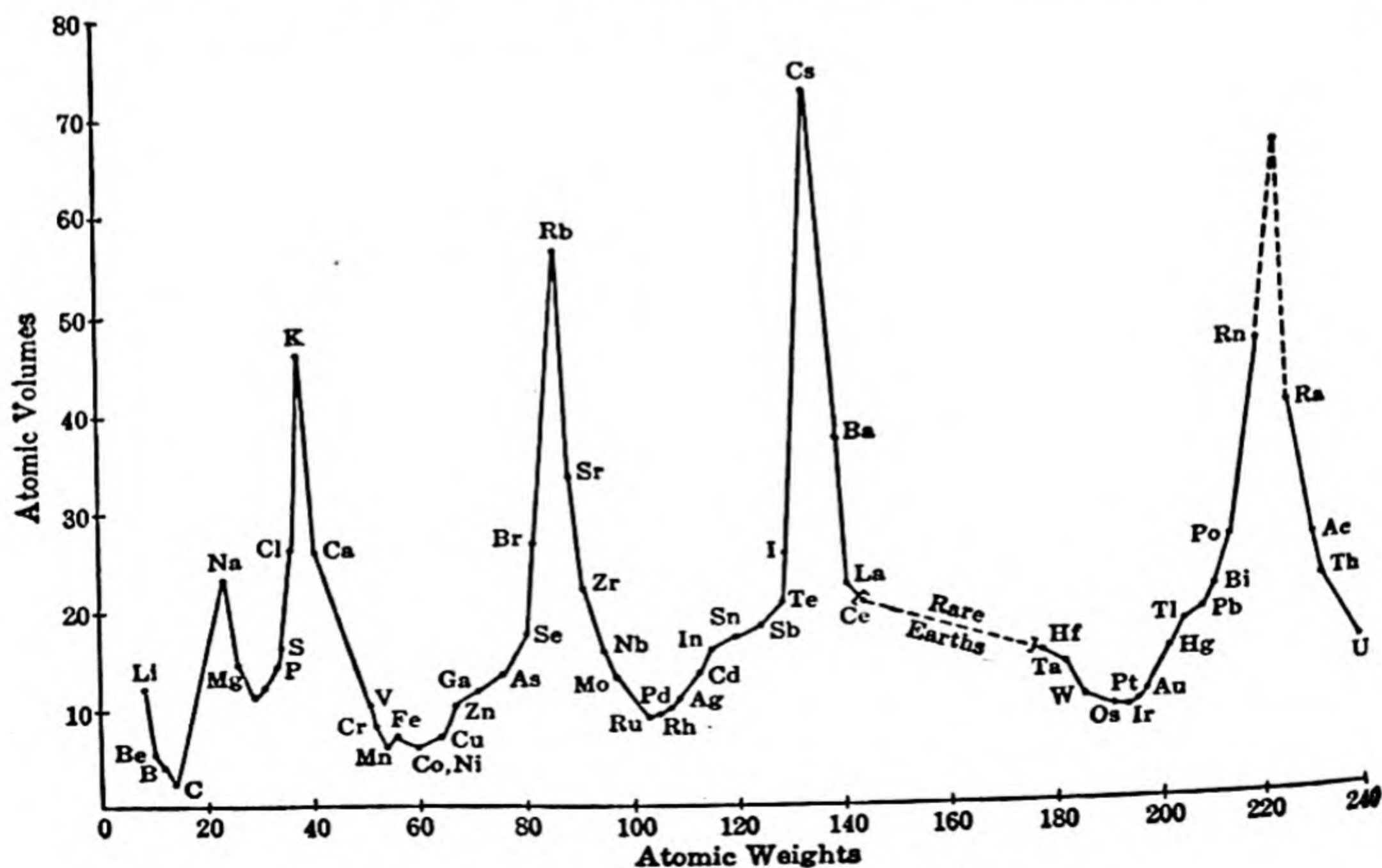
Fig. 58. Periodic Curve of Atomic Volumes

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by Lothar Meyer. The significance of a periodic function is shown in Fig. 58, in which atomic volumes are plotted against atomic weights, as done by Meyer. The atomic volume is equal to the atomic weight divided by the density of the solid element.

Recognizing the existence of elements not discovered, and leaving blanks to indicate the spaces they should occupy, Mendeléef arranged the known elements in a table according to their natural groups. In some instances, the order of the atomic weights seemed to be incorrect according to the properties. It was assumed that the atomic weight determinations were erroneous in such instances, and the order was inverted, placing the elements in the groups indicated by their properties.

A modified form of the periodic system, arranged according to the principle stated by Mendeléef, is shown in Table 14. The elements are represented by their symbols, and the atomic weights are written beneath the symbols. Hydrogen is placed alone as the only element in the first row at the top of the table. The next eight elements, helium to fluorine, are in the second row, each being the first element in Columns 0–VII, except lithium which follows hydrogen in Column I. The following eight elements, neon to chlorine, are in the third row, and are arranged in appropriate columns under the corresponding elements of the second row, i.e., neon in the column with helium, sodium with lithium, etc. The next complete period contains eighteen elements, argon to bromine, and therefore the plan of the arrangement is changed. Those from argon to manganese fall into the groups already established, but the elements from scandium to manganese are listed at the other side of the appropriate columns as first members of subgroups. Iron, cobalt, and nickel are placed together in the ninth column, Group VIII, as a closely related triad of elements. The remaining elements of this long period are entered in Groups I–VII; copper and zinc being shown as the first members of subgroups in Groups I and II. By continuing this arrangement, the fifth and sixth long periods are completed, and a seventh period is started.

The elements in each of the Groups I–VII are distributed into two columns, the main group and the subgroup. The resemblance of the elements in a subgroup to one another is not nearly as close

TABLE 14. PERIODIC SYSTEM BASED ON ATOMIC WEIGHTS (SHORT FORM)

Period ↓ / Group →	0	I	II	III	IV	V	VI	VII	VIII		
I		H 1.008									
II Short	He 4.0	Li 6.9	Be 9.0	B 10.8	C 12.0	N 14.0	O 16.0	F 19.0			
III Short	Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5			
IV Long	A 39.9	K 39.1	Ca 40.1	Sc 45.1	Ti 47.9	V 51.0	Cr 52.0	Mn 54.9	Fe 55.8	Co 58.9	Ni 58.7
		Cu 63.6	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79	Br 79.9			
V Long	Kr 83.7	Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Cb 92.9	Mo 96.0	Ma —	Ru 101.7	Rh 102.9	Pd 106.7
		Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9			
VI Long	Xe 131.3	Cs 132.9	Ba 137.4	La 138.9	Hf 178.6	Ta 180.9	W 184.0	Re 186.3	Os 191.5	Ir 193.1	Pt 195.2
		Au 197.2	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0	Po 210	—			
VII Incomplete	Rn 222	—	Ra 226.0	Ac 226?	Th 232.1	Pa 231	U 238.1				

Atomic weights are given to the first decimal place.

Fourteen elements are omitted from this classification. These elements together with lanthanum are the *rare earths*. Their symbols and atomic weights are: Ce, 140.1; Pr, 140.9; Nd, 144.3; Il, —; Sm, 150.4; Eu, 152.0; Gd, 156.9; Tb, 159.2; Dy, 162.5; Ho, 163.5; Er, 167.6; Tm, 169.4; Yb, 173.0; Lu, 175.0.

as in the main group. There are fourteen elements between lanthanum and hafnium, in order of atomic weights, which do not fit into this scheme and are listed in a footnote to the table.

The discrepancies between the order of some elements when judged by their properties and when arranged according to accepted values of their atomic weights are mentioned in a preceding paragraph. The recognition of such discrepancies has led to redetermination of atomic weights and to correction of errors in previously accepted values. Three pairs of elements, however, must remain in the inverted order of their atomic weights to fit into the proper groups. These are argon and potassium, cobalt and nickel, and tellurium and iodine.

The Long Form of the Periodic Table. A number of different forms of the periodic table have been proposed. Each classification is an empirical arrangement based on the atomic weights and the properties of elements, and different forms serve to emphasize specific relationships. The expanded form of the table, shown in Table 15, is a very useful arrangement. This table contains eighteen columns, so as to provide a space for each element in the long periods. The first row contains two elements, hydrogen in the first column and helium in the last. The second row contains the eight elements, lithium to neon. Lithium is listed in the first column under hydrogen, and beryllium in the second column. The remaining six elements are listed in the last six columns, bringing neon in the column with helium. The next eight elements in order of their atomic weights, sodium to argon, are listed according to the same scheme. Argon is clearly the eighth member of this group, even though the atomic weight of potassium follows chlorine, for argon is an inert gas and potassium is an alkali metal. There are eighteen elements in the fourth period, and they are listed appropriately in the fourth row across the table. The ten elements, scandium to zinc, denote one member in each of the groups not represented in the preceding periods. The remaining elements are listed as the fifth, sixth, and incomplete seventh periods. The first two columns are numbered I and II, and the last six from III to VIII. The intervening columns are designated from III–B to VIII–B and from I–B to II–B.

TABLE 15. PERIODIC CLASSIFICATION OF THE ELEMENTS (LONG FORM)

Group → / Period ↓	I	II	III-B	IV-B	V-B	VI-B	VII-B	VIII-B	VIII-B	VIII-B	I-B	II-B	III	IV	V	VI	VII	VIII
I — 2 Elements	H 1.008																	He 4.003
II — 8 Elements	Li 6.94	Be 9.02											B 10.82	C 12.01	N 14.008	O 16.000	F 19.00	Ne 20.18
III — 8 Elements	Na 22.997	Mg 24.32											Al 26.97	Si 28.06	P 30.98	S 32.06	Cl 35.46	A 39.94
IV — 18 Elements	K 39.10	Ca 40.08	Sc 45.10	Ti 47.90	V 50.95	Cr 52.01	Mn 54.93	Fe 55.85	Co 58.94	Ni 58.69	Cu 63.57	Zn 65.38	Ga 69.72	Ge 72.60	As 74.91	Se 78.96	Br 79.92	Kr 83.7
V — 18 Elements	Rb 85.48	Sr 87.63	Y 88.92	Zr 91.22	Cb 92.91	Mo 95.95	Ma —	Ru 101.7	Rh 102.91	Pd 106.7	Ag 107.88	Cd 112.41	In 114.76	Sn 118.7	Sb 121.76	Te 127.61	I 126.92	Xe 131.3
VI — 32 Elements	Cs 132.91	Ba 137.36	La[a] 138.92	Hf 178.6	Ta 180.88	W 183.92	Re 186.31	Os 190.2	Ir 193.1	Pt 195.23	Au 197.2	Hg 200.61	Tl 204.39	Pb 207.21	Bi 209.0	Po —	—	Rn 222
VII — 6 Elements	—	Ra 226.05	Ac —	Th 232.12	Pa 231	U 238.07												

— Transition Elements —

[a] Rare Earth Elements	Ce 140.1	Pr 140.9	Nd 144.3	Il —	Sm 150.4	Eu 152	Gd 156.9	Tb 159.2	Dy 162.5	Ho 164.9	Er 167.2	Tm 169.4	Yb 173	Lu 175

Periods of Elements. A period consists of elements occupying a horizontal row in the expanded or long form of the periodic table. Each period, after the first, begins with an alkali metal and ends with an inert gas, except the seventh period which is incomplete. The elements in Group I are active metals and in Group VII active nonmetals. Each period contains elements showing a transition from metal to nonmetal. This change from active metal to active nonmetal is not abrupt, but elements showing intervening properties afford a series of steps. In the first period, lithium is an active metal while beryllium is less strongly metallic in properties. Boron exhibits the properties of a nonmetal of low activity, and the nonmetal character of the element becomes successively more pronounced through carbon, nitrogen, and oxygen to fluorine. After an intervening inert gas, there is a repetition, except that the transition takes place one column further to the right. Sodium, magnesium, and aluminum are metals whose activities decrease in the order given. Silicon, phosphorus, sulfur, and chlorine are nonmetals with consecutively increasing nonmetal activity. The elements in the B groups show irregularities in their relationships, so that they are called transition elements. There is greater resemblance among successive transition elements of a period than among the elements in the main groups. This is particularly noticeable toward the center of the table. In the fourth period, for example, iron, cobalt, and nickel resemble each other very closely, and the difference from manganese on one side and copper on the other is less than between some of the successive elements in the main groups.

Groups of Elements. In preceding chapters, the similarities of the metals within Group I and of the nonmetals within Group VII have been emphasized. *The elements in a main group closely resemble one another in properties.* They react in a similar manner with the same substances and yield compounds which are also similar. Thus, the hydroxides of the alkali metals are actively basic in properties, and the hydrides of the halogens are acidic. The halides of the alkali metals are similar binary salts.

An important similarity shown by the elements in each main group is in their valence states. The limiting value of the positive valence is the same as the group number for the elements in the main groups, although these maximum values do not necessarily

apply to all of the elements in each group. Fluorine, for example, does not form compounds in a 7+ valence state. Other positive valence states are also shown, particularly by some elements in the high-numbered groups. Usually the most important valences are even numbers for the elements in the even-numbered groups, and odd numbers for elements in odd-numbered groups. The most important positive valences of sulfur are 4+ and 6+, while chlorine yields compounds in the 1+, 3+, and 5+ states in addition to 7+. Negative valences are shown by nonmetallic elements in compounds with hydrogen, with metals, and with less active nonmetals. The limiting value is 4− for the elements in Group IV, and decreases for each succeeding group to 1− for the elements in Group VII. In the subgroups, valences corresponding to the group numbers are not always significant. The valences 2+ and 3+ are common among the transition elements.

A second general relationship already discussed is that, although the elements in each group differ in activity, they exhibit a regular pattern of change when arranged in order of atomic weight. In general, the activities of the metals in a main group increase in the order of the atomic weights. The activities of nonmetals in a group commonly decrease with increasing atomic weight.

A number of blanks were left in the table arranged by Mendeléef. He assumed that elements existed which would fit into these spaces. On the basis of the general relationships inherent in the classification, he made predictions concerning the properties of some of these missing elements. This proved to be a great aid in the search for missing elements. In 1871, Mendeléef predicted the properties of three missing elements, which he called eka-boron, eka-aluminum,

TABLE 16. PREDICTED AND OBSERVED PROPERTIES OF GERMANIUM

	Eka-silicon	Germanium
Atomic weight	72	72.5
Specific gravity	5.5	5.47
Color	Dirty-gray	Grayish white
Oxide	Dioxide	GeO_2
Specific gravity of oxide	4.7	4.703
Chloride	Tetrachloride	$GeCl_4$
Boiling point of chloride (° C.)	Below 100	86

and eka-silicon. Within fifteen years, each of these elements was discovered: scandium in 1879, by Nilson; gallium in 1875, by Boisbaudron; and germanium in 1886, by Winkler. The remarkably close agreement between the properties predicted in advance and those actually observed indicates the usefulness of this system in the classification of elements. In Table 16 the properties predicted by Mendeléef are described under the name *eka-silicon* and those determined experimentally after the discovery of the element, under the name *germanium*.

Defects in the Periodic System. Although the value of this system of classification is great, in some respects it fails to be fully satisfactory. The relation of hydrogen to the various groups is uncertain. Only one or two of the valence states of the elements in the groups can be readily correlated with the position of the element in the table, and other valence states may be more significant, particularly in the subgroups. No relation between the activities of the elements in different groups is apparent from the system. Fifteen elements, known as *rare earths*, with atomic weights between those of barium and hafnium, do not fit into the scheme. These elements show characteristically the positive valence 3, except that cerium also has a valence 4. They are so similar to each other in chemical properties that separations are difficult. These fifteen elements appear to occupy the position of a single element in the Mendeléef system of classification, and their properties do not permit distribution in series throughout the other groups. These elements are rare, and few of them have practical importance.

The periodic system of Mendeléef is based on experiment and does not explain the arrangement of the elements. Mendeléef had little sympathy with attempts to attach metaphysical meaning to the periodic relationships but insisted that the classification was strictly empirical in its basis. Naturally, however, the student desires to know why the elements show differences in their properties and activities and why periodic repetition in properties occurs. The interpretation of the periodicity of elements was not possible until the composition and structure of the atoms had been fully ascertained by the accumulation of a sufficiently large body of experimental data.

EXERCISES

1. State fully the meaning of the periodic law.
2. What practical advantage does the periodic system afford in the study of the elements?
3. Using the halogens and the alkali metals as examples, show how the properties of the elements vary within a group.
4. Noting the gradation in the properties of the elements in a group, predict the properties of the missing element in the fifth period of Group VII.
5. Sodium in Group I is an active metal and chlorine in Group VII, an active nonmetal. What general relationship would you expect to find among the elements, which fall between sodium and chlorine in atomic weights, in Groups II–VI?
6. How has the periodic system aided in correcting the atomic weights of the elements?
7. How has the periodic system aided in the search for missing elements?
8. Mention some imperfections of the periodic system based on atomic weights.

SUPPLEMENTARY READINGS

Jaffe, B., *Crucibles*, Simon and Schuster, Inc., New York, 1930, sec. XI.

Moore, F. J., *History of Chemistry*, McGraw-Hill Book Company, Inc., New York, 1939, chap. XVI.

Harrow, B., *Eminent Chemists of Our Time*, D. Van Nostrand Company, New York, 1920.

Weeks, M. E., *The Discovery of Elements*, Journal of Chemical Education, Easton, Pa., 1935, chaps. XIV–XV.

Venable, F. P., *The Development of the Periodic Law*, Chemical Publishing Company of New York, Inc., New York, 1896.

Mendeléef, D. I., "The Periodic Law of the Chemical Elements," *J. Chem. Soc.* **55**, 634 (1889).

Reinmuth, O., "The Periodic Classification of the Elements," *J. Chem. Education* **5**, 1312 (1928).

Foster, L. S., "The Periodic Table," *J. Chem. Education* **16**, 409 (1939).

Chapter 13

ATOMIC STRUCTURES

For nearly a century after Dalton formulated the atomic theory, atoms were generally assumed to be the indivisible particles of the elementary substances. Early determinations seemed to indicate that all atomic weights were integral multiples of the atomic weight of hydrogen. In 1815, Prout, seeking a relation between the properties of the elements and their atomic weights, suggested the hypothesis that atoms of hydrogen might be the fundamental units of which all atoms are composed. The more accurate determination of atomic weights by Berzelius and by Stas showed clearly that many atomic weights bear no simple integral relationship to the atomic weight of hydrogen and led to the conclusion that Prout's hypothesis was unfounded. Nevertheless, the relationships stated in the periodic law demonstrate that there is a connection between chemical properties of the elements and successive increments in the weights of their atoms. Although Prout's hypothesis was not accepted and was far beyond the experimental resources of his day, it agrees in modified form rather closely with some of the modern ideas dealing with the constitution of atoms. It has been found that a small number of fundamental particles, possibly only three, are sufficient to serve as structural units of the atoms and to account for their behavior.

Cathode Rays. The Electron. The nature of one of the structural units of atoms has been determined by investigating effects that accompany the passage of electricity through gases at low pressures. The conductivity of electricity by rarefied gases was discovered by Plücker in 1859. An electrical discharge through air at ordinary pressures requires very high voltage, and is intermittent, taking the form of a succession of sparks. If the electrodes are sealed into a glass tube and the air is pumped out, it is found that the required voltage becomes less as the density of the gas in

the tube decreases until very low pressures are reached. At a pressure of one millimeter or less, there is a continuous flow of the current, and beautiful color effects may be observed. At a pressure of 0.01 mm., the luminous column in the tube disappears and a greenish light originates in the walls of the tube. Familiar applications of the color effects accompanying the passage of electricity through gases are sodium and mercury vapor lights, and the use of neon at low pressures for display signs.

The nature of the radiation that produces the effects observed during the passage of electricity through rarefied gases was investigated by Hittorf, Crookes, Thomson, and many others. The rays originate at the cathode, the negative electrode, and travel in straight lines at right angles to the surface of the cathode. Hence, they are known as *cathode rays*. They cause the emission of light by some of the materials which they strike, a phenomenon called fluorescence. The rays have low penetrating power, so that a piece of metal placed in their paths causes a corresponding shadow on the wall of the tube. (Fig. 59.) The rays may be brought to a focus by the use of a concave cathode, and metals placed at this focus become heated to a high temperature, proving that the rays carry energy. The cathode rays penetrate thin metal foil. Tubes may be constructed which permit the rays to emerge. If they are allowed to fall on a photographic plate, they cause decomposition of silver salts. Furthermore, the rays produce electrically charged particles, gas ions, in air, thus permitting the rapid loss of charge when they are brought into the air near the knob of a charged electroscope. (Fig. 60.)
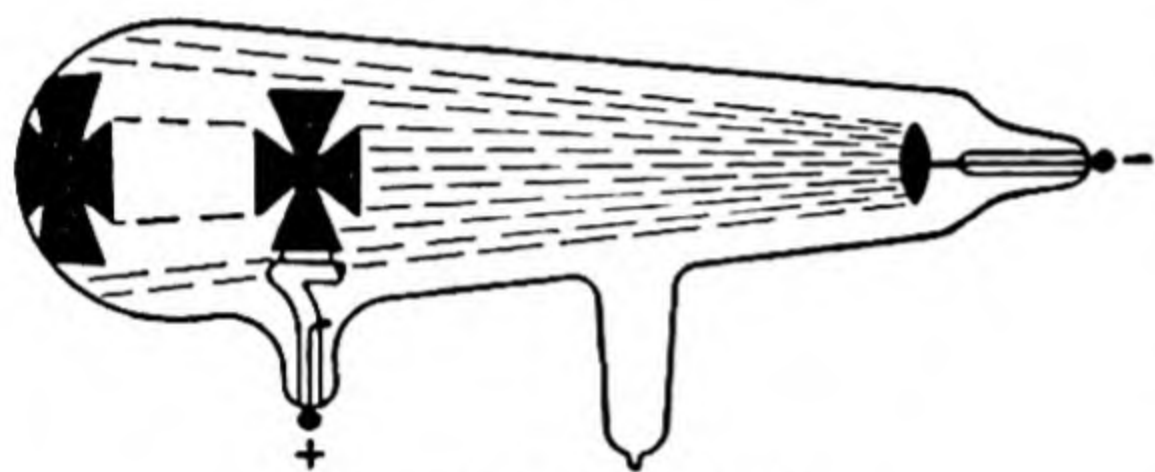
Fig. 59. Cathode Rays
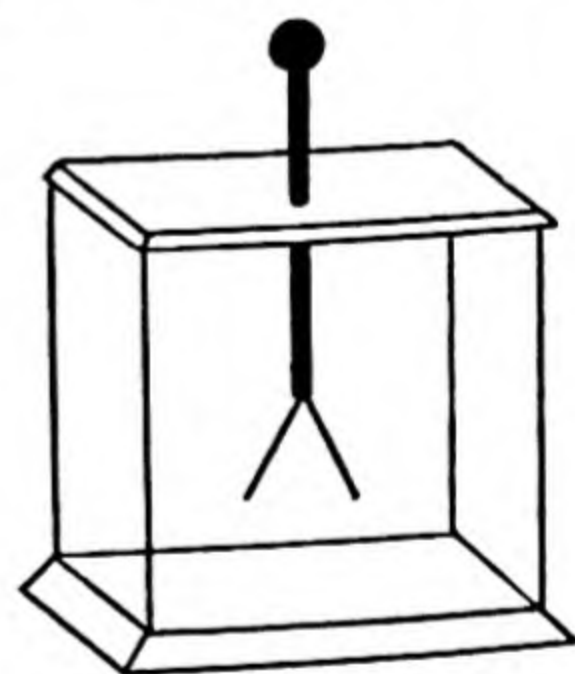
Fig. 60. Electroscope

A beam of rays, subjected to the action of a magnetic or an electrical field, is deflected in a direction which shows that it consists of rapidly moving negatively charged particles. (Fig. 61.) The nature of these particles has been determined experimentally.

They have a mass equal to 1/1845 times that of the hydrogen atom or 9×10^{-28} g. This weight is 0.00054 on the atomic weight scale. The electrical charge of the cathode ray particle is 1.59×10^{-19} coulombs. This charge is identical in amount and opposite in sign
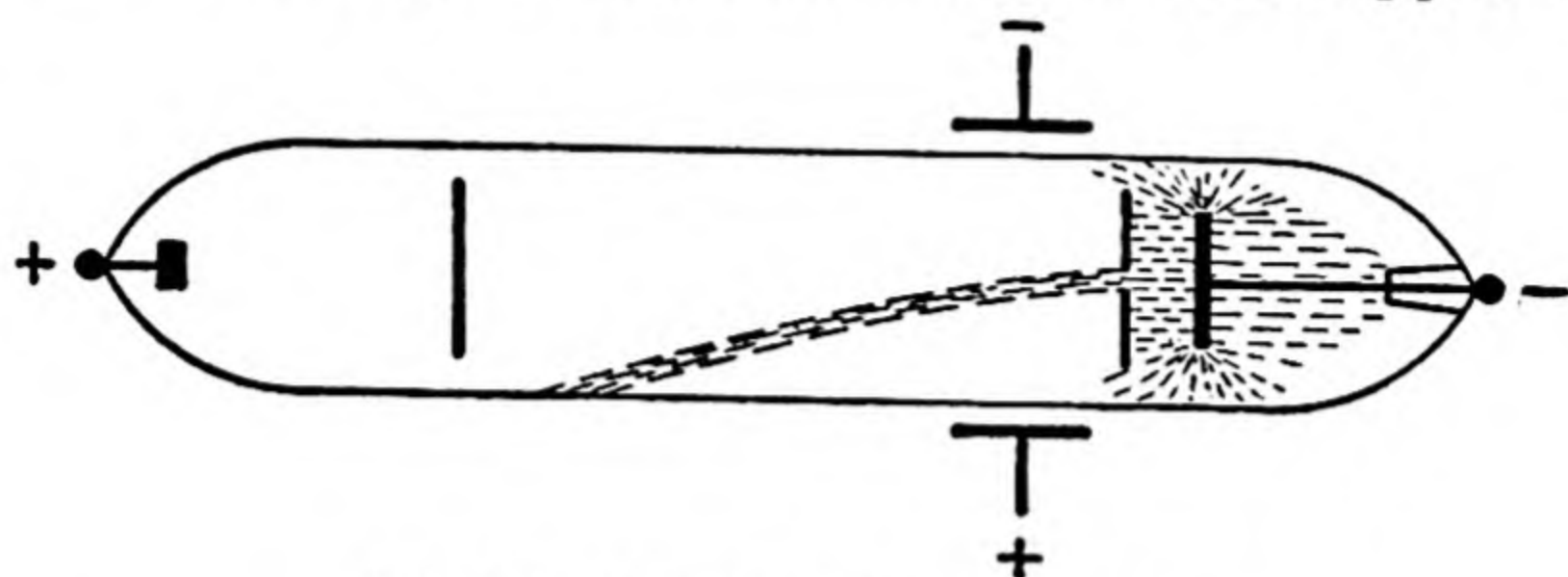
Fig. 61. Deflection of Cathode Rays

to the charge of the hydrogen ion. The particles in the cathode rays are identical with "the natural unit of electricity" to which Stoney gave the name electron in 1891. Consequently, the electron is the unit charge of negative electricity.

Positive Rays. In 1886, Goldstein, using a tube with a perforated cathode, observed a band of light passing through the cathode into the region away from the anode. (Fig. 62.) These rays consist of positively charged particles having atomic magnitude and moving with velocities much lower than the electrons in cathode rays. The charge of these particles is either one unit of positive charge or an integral multiple of the unit charge. They possess the atomic mass of the residual gas in

Fig. 62. Canal Rays

the tube and are gas ions. Consequently, the assumption is made that the particles in the positive rays are formed by removal of one or more electrons from the atoms and that *electrons are common constituents of the atoms of the elements.* The lightest of the positive ray particles is formed when hydrogen is the residual gas in the tube. This particle is considered to be a second fundamental unit of matter because the masses of all other positive ray particles are multiples of that of hydrogen if allowance is made for the loss of mass caused by the formation of the more complex particles. Rutherford suggested the name *proton* for this particle.
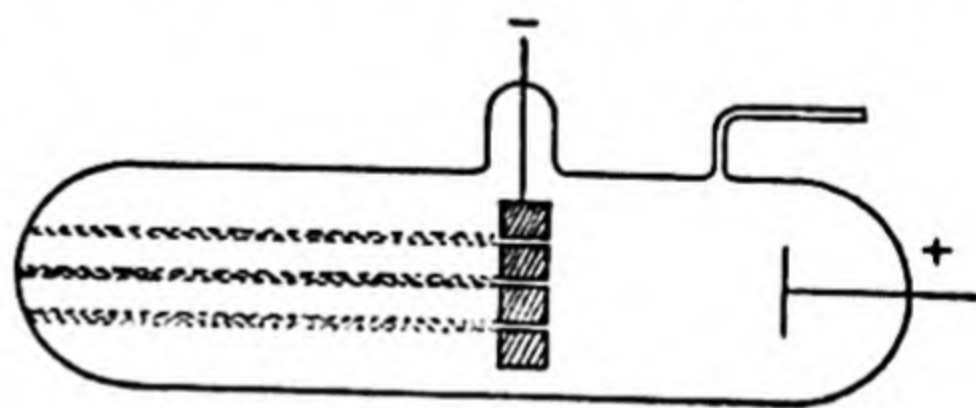
In the free condition, it has an atomic mass of 1.0076 and a positive electrical charge of one unit.

Röntgen Rays. X-Rays. In 1895, Röntgen discovered a third type of radiation originating in cathode ray tubes. These rays are not deflected by electric or magnetic fields. They have great penetrating power, passing readily through the walls of the tube. They affect photographic plates, cause ion formation in air, and produce fluorescence in materials such as zinc sulfide. These rays, commonly called X-rays, are electromagnetic waves of the same nature as light, but they have much shorter wave length. They originate when high speed electrons strike a dense material. In the X-ray tube the cathode rays converge to strike an oblique target, the anticathode, made of a metal of high density such as tungsten.

The determination of the wave length of light is based on the use of a diffraction grating consisting of a large number of opaque lines at exactly equal distances apart. When the distance between these lines bears the correct relation to the wave length of the light passing through the grating, a series of bright and dark lines is obtained, because of the interference of the waves spreading out from the slits between the opaque lines. Where the crest of one wave meets the crest of another, the two reinforce each other, producing a bright line. The angle at which the waves from the different slits reinforce one another depends on the relation between the wave length of the light under examination and the distance between the slits. The wave lengths of X-rays are so short that it is not possible to rule lines close enough for a grating to cause their diffraction. In 1912, however, Laue discovered that thin crystals may be used as diffraction gratings for X-rays, thus making possible the calculation of the wave lengths. The radiation from an X-ray tube is usually complex, but certain specific wave lengths are characteristic of the substance of the target, or anticathode. The property of penetrating many substances opaque to ordinary light is the basis of the better known uses of X-rays. They penetrate substances of low density more readily than substances of high density.

Radioactive Elements. In 1896, Becquerel observed that uranium salts emit a radiation that affects the photographic plate, even when it is protected from ordinary light by a wrapping of black paper. These radiations also cause the formation of gas ions

in air, indicated by the loss of charge when a uranium salt is placed near the knob of a charged electroscope. The emission of penetrating radiations by chemical substances is called *radioactivity*. The elements emitting such radiations are the radioactive elements.

It was observed subsequently that the activity of the radiations from uranium compounds is proportional to the percentage of uranium they contain. Uranium ores exhibit an activity greater than accounted for by their uranium content. Madame Curie and her husband, M. Pierre Curie, observed the emission of radiations by pitchblende residues from which uranium has been extracted, and they soon discovered a new radioactive element, which they named *polonium*. After long and painstaking work they prepared a compound from uranium minerals, a million times more active than uranium. The active element in this compound was given the name *radium*. Madame Curie isolated the element in 1910. Radium is always present in uranium ores. The ratio between the amounts of radium and uranium in these ores is constant, only one part of radium to three million parts of uranium.

Radiations from the Radioactive Elements. Three types of radiation are emitted by the mixture of compounds of uranium and the other radioactive elements associated with it. These radiations are analogous to those observed during the passage of electricity at high potential through rarefied gases.

Beta rays consist of a stream of electrons, identical with the cathode ray particles. These particles are discharged from radioactive substances with different velocities depending on the source, but ranging from 30–95 per cent of the velocity of light. They have relatively high penetrating power.

Alpha rays are composed of positively charged particles having a mass almost four times as great as the proton and a charge twice as great. Except for the charge, they are identical with helium atoms, and an alpha particle becomes an atom of helium when it gains two electrons. The velocity of the alpha particles is approximately one tenth of the velocity of light. Alpha particles have such small penetrating power that they are stopped by a thin foil of metal and are able to pass through but a few centimeters of air at ordinary pressures. They affect the photographic plate, cause the formation of gas ions in air, and produce fluorescence in many minerals.

Gamma rays, the most penetrating of the radiations from radioactive elements, pass through thick layers of metals. They do not suffer deflection in magnetic or electrical fields. They are of the same nature as X-rays, except still shorter in wave length. The wave lengths of some of the well-known radiations of electromagnetic nature in Ångstrom units* are: gamma rays, 0.010–1.40; X-rays, 10–150; ultraviolet, below 4000; visible spectrum, 4000–7000; infrared, greater than 7000; Hertzian waves, 2.2×10^6. It is considered probable that gamma rays originate as the result of the mutual annihilation of the electron and the positron, a second particle of low mass and high energy, discussed briefly in a subsequent paragraph. Both particles disappear in this change, being converted into gamma radiation.

Source of Alpha and Beta Particles. Soon after the discovery of radioactivity, the investigation of the nature of the radiations led Madame Curie to conclude that *radioactivity is a property of the atoms of the radioactive elements*. A particular variety of radioactive atom characteristically emits only one kind of particle, but a mixture of the atoms of two radioactive elements may emit both kinds. Thus, radium atoms disintegrate to form the radioactive gas radon and alpha particles.

$$\text{Radium} \longrightarrow \text{Radon} + \text{Alpha particle}$$
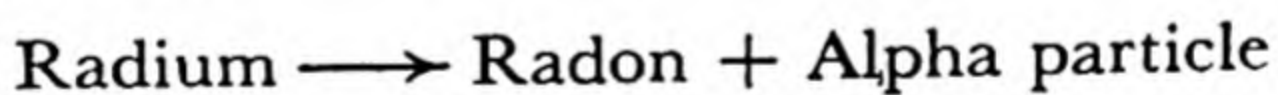
Soddy demonstrated that a pure uranium compound at first exhibits only one kind of radiation, but the material gradually begins to show all three kinds. This indicates that the uranium compound contains only one variety of radioactive atom and that other radioactive elements are produced as changes occur. McCoy demonstrated the presence of radium in all uranium ores and Boltwood, the presence of radon. From these observations it appears that the emission of either an alpha or a beta particle causes one variety of atom to change into another. In this way a series of radioactive elements is formed from uranium. In 1902, Rutherford and Soddy advanced the disintegration theory of radioactivity: *The atoms of the radioactive elements are complex, and they spontaneously disintegrate with the emission of alpha and beta particles and the formation of other complex atoms.*

* One Ångstrom unit is 1×10^{-8} cm. or 3.937×10^{-9} in.

Only a certain definite proportion of the atoms in a sample of any radioactive substance undergoes decomposition in a given period of time. Only one out of 100 million atoms of radium decomposes per second. Consequently, an infinite length of time would be required for the complete decomposition of a sample. No changes in conditions to which the substance may be subjected, either chemical or physical, have been found to affect the rate of the radioactive change or the nature of the products. From the rate of disintegration, the time required for the decomposition of one half of a sample may be calculated. This time is known as the *period* of the element. The periods of radioactive elements vary from a few seconds to billions of years. Nuclear transformations are attended by the evolution of enormous amounts of energy compared to the changes in chemical processes. Radium evolves energy at a rate equivalent to 137 calories per gram during each hour and continues at this rate throughout its entire life.

Disintegration Products of the Radioactive Elements. There are a number of radioactive elements in the *uranium series*. The spontaneous disintegration of the atoms leads successively to the formation of each element from its predecessor. Alpha particles are emitted during some of these changes and beta particles during others. The relations of these elements are shown in Table 17.

The significance of the atomic numbers will be discussed in a subsequent paragraph.

TABLE 17. DISINTEGRATION PRODUCTS OF URANIUM

Substance	Atomic Number	Atomic Weight	Particle Ejected	Period
Uranium I	92	238	Alpha	4.5×10^9 years
Uranium X_1	90	234	Beta	24.5 days
Uranium X_2	91	234	Beta	1.14 minutes
Uranium II	92	234	Alpha	2×10^6 years
Ionium	90	230	Alpha	7.6×10^4 years
Radium	88	226	Alpha	1590 years
Radon	86	222	Alpha	3.8 days
Radium A	84	218	Alpha	3.0 minutes
Radium B	82	214	Beta	26.8 minutes
Radium C	83	214	Beta	19.5 minutes
Radium C'	84	214	Alpha	1×10^{-4} seconds
Radium D	82	210	Beta	25 years
Radium E	83	210	Beta	4.85 days
Polonium	84	210	Alpha	136 days
Lead	82	206		Stable

Transmutation of Elements. The spontaneous changes radio-active elements undergo cause the transformation of one variety of element into another, a change known as transmutation of elements. In 1919, Rutherford and Chadwick caused the transmutation of elementary nitrogen by subjecting it to the action of alpha particles. Oxygen and hydrogen are the products of this change. More recently, a large number of transmutations have been effected. Many of the atoms produced in this manner are radioactive. The transmutation of the elements results from changes in the constitution of the atoms. Therefore, it must be concluded that atoms of all elements, not merely of the radioactive elements, are complex.

Detection of High Velocity Particles. One of the most effective methods of detecting these particles is based on the formation of
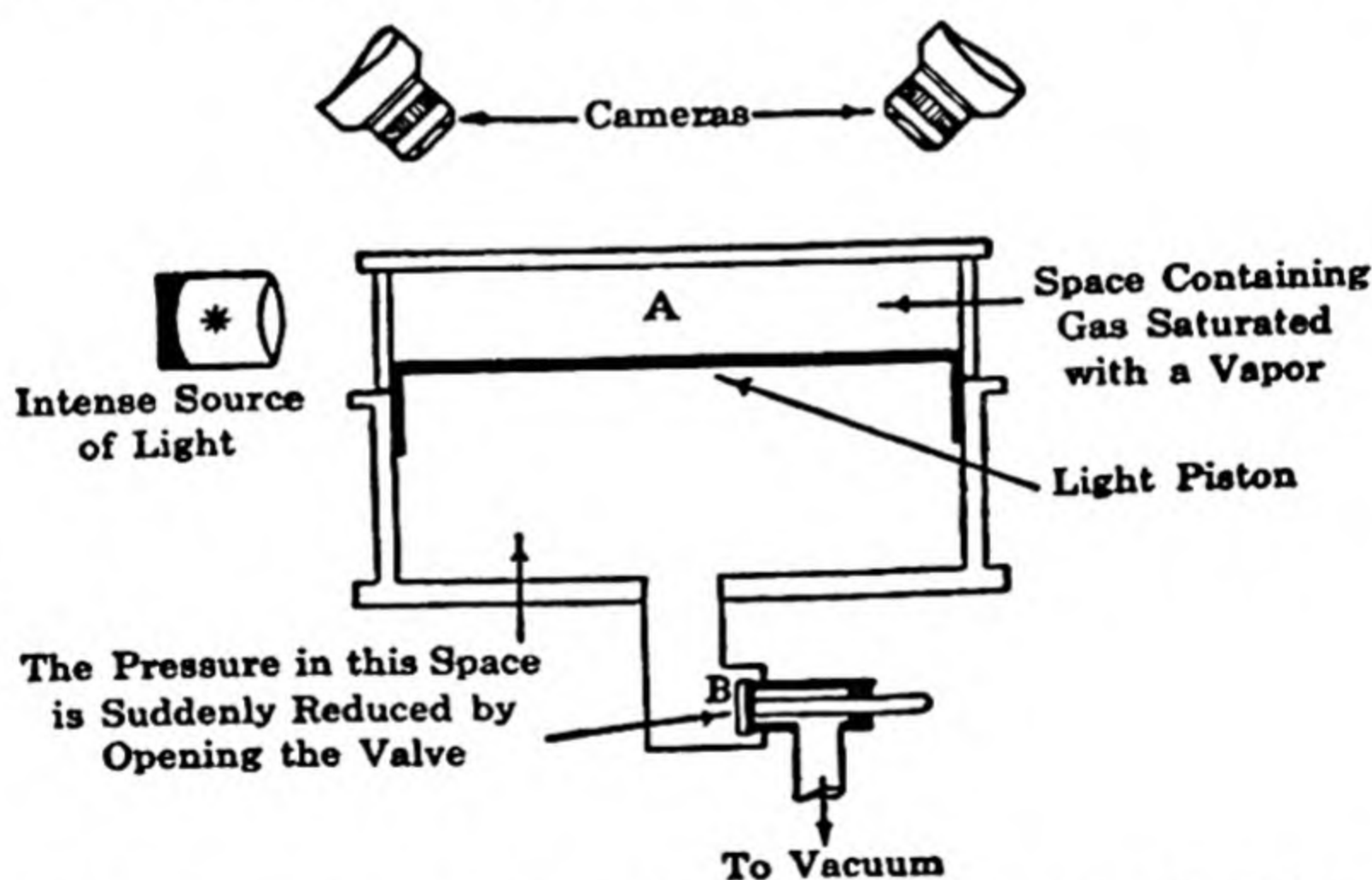
Fig. 63. The Wilson Cloud Chamber. (From Rutherford, *The Newer Alchemy*)

The chamber, A, of the cylindrical vessel contains dust-free air saturated with water vapor. When the light piston is suddenly lowered, the gas expands and is cooled, thus becoming supersaturated. The formation of gas ions in this space causes the condensation of water in minute droplets.

gas ions. Experiments devised by C. T. R. Wilson permit the observation of the path of an individual charged particle through a gas. (Fig. 63.) Alpha particles, given off by a radioactive material, cause the formation of gas ions along their paths. These ions serve as nuclei for the condensation of water vapor in a supersaturated space, thus making the paths visible as fog tracks. A photograph

of the tracks of alpha particles, produced in this manner, is shown in Fig. 64. The track ends abruptly when the velocity of the particle has become so low that it no longer produces gas ions.
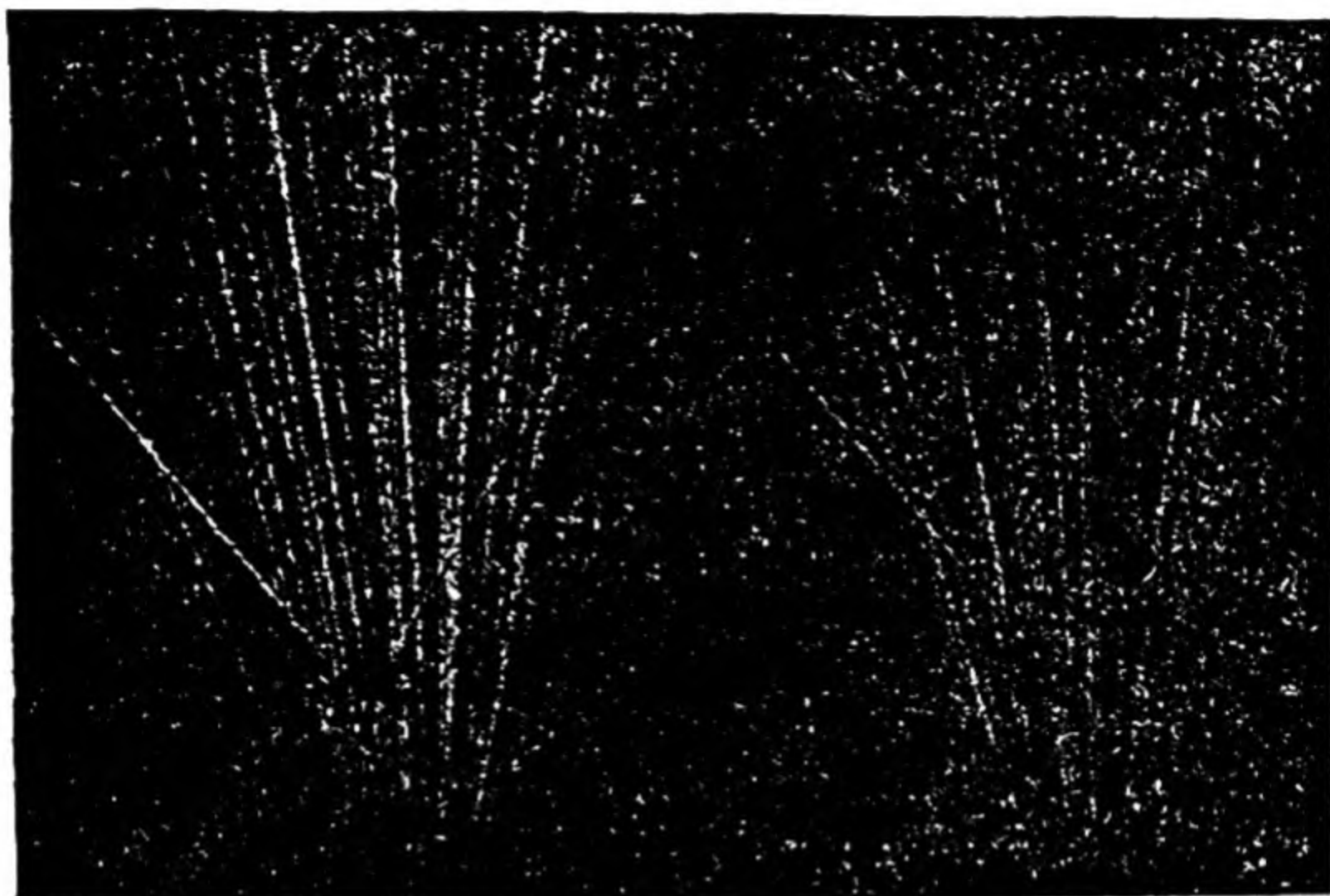
Fig. 64. Tracks of Alpha Particles. The effect of a collision with a helium atom is also shown. (Professor P. M. S. Blackett, Cavendish Laboratory)

The track caused by the beta ray in the cloud chamber is much less dense than the alpha ray track because it produces a smaller number of gas ions along the way. Beta ray particles have small mass and are easily deflected from a straight line. Electrically neutral particles leave no visible path as they move rapidly through a supersaturated space, because they do not cause the formation of gas ions.

The Neutron. The existence of neutral particles as units of atomic structure was suggested by Rutherford in 1920. The detection of neutral particles is difficult because they do not affect a charged electroscope and do not leave a fog track in the cloud chamber. It was observed in 1930 that the bombardment of beryllium by alpha particles from polonium gives rise to a very energetic type of radiation. This radiation was first thought to consist of gamma rays, but the energy relationships were found to disagree with this assumption. In 1932, Chadwick showed that this radiation consists of neutral particles having approximately the same mass as the proton. Although a neutral particle does not leave a track as it passes through the cloud chamber, it may cause the formation

of charged particles by striking the center of a gas atom. The charged particles formed in this manner then produce gas ions and cause a fog track. The neutral particle formed during certain atomic disintegrations is called a *neutron*. It has an atomic mass of 1.009.

The Positron. A positively charged particle having the mass of the electron was discovered by Anderson in 1932. He first observed the path of this particle in photographs of fog tracks produced by the action of cosmic rays on certain atoms. This particle appears to originate during the energy changes which accompany the
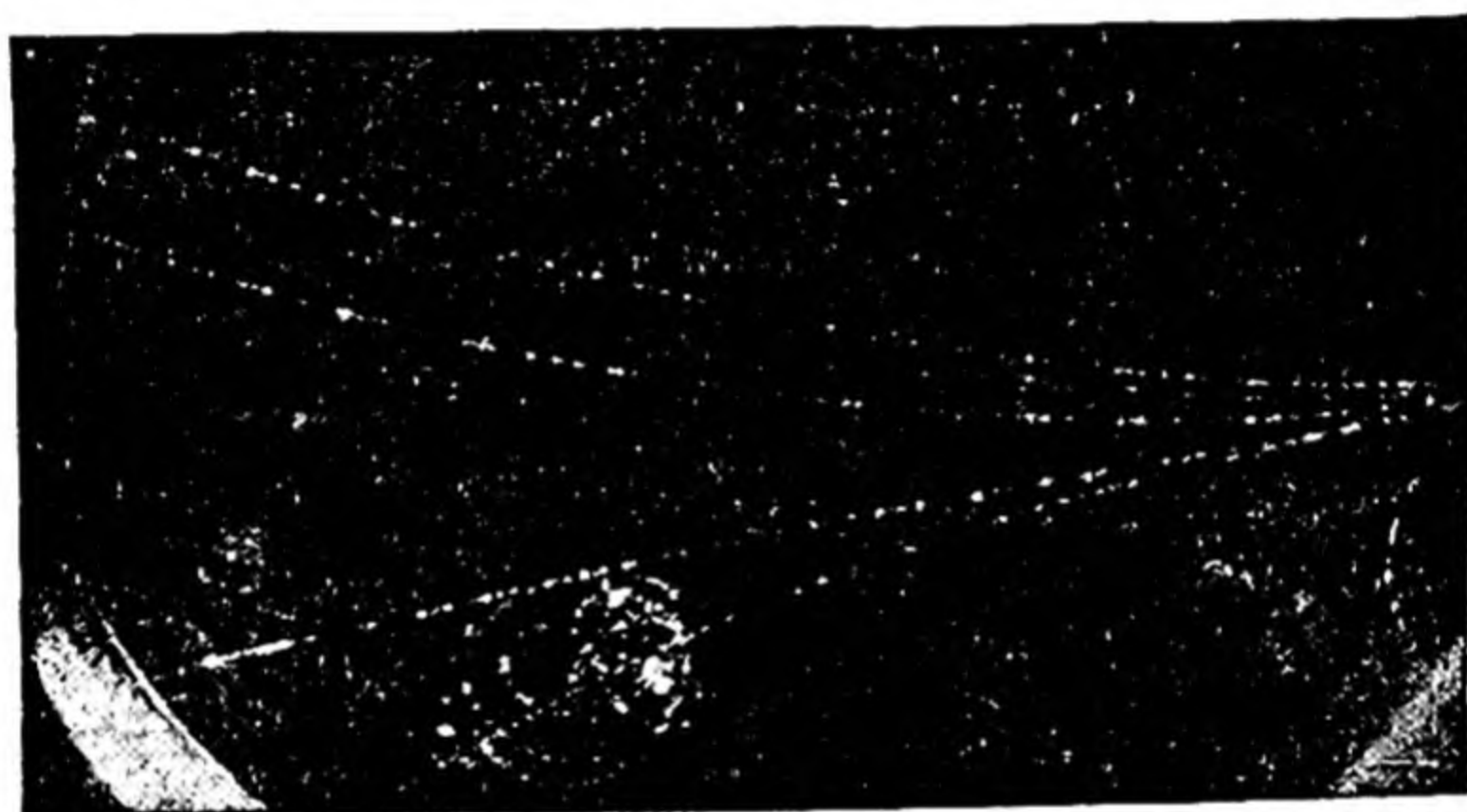
Fig. 65. *Tracks of Electrons and Positrons. (Professor Carl D. Anderson, California Institute of Technology)*

Particles originating at the same point at the left of the picture pass through the cloud chamber where they are subjected to a magnetic field. They are deflected in opposite directions.

decomposition of certain atoms. Since the electron and positron have the same mass and have charges of similar magnitudes but opposite signs, they are deflected to the same degree but in opposite directions in a magnetic field. (Fig. 65.)

Unit Particles of Atomic Structure. The existence of minute particles — negative, neutral, and positive — in the atoms of the elements is now considered to be fully established. Five particles, which might serve as units, have been described in the preceding paragraphs, *viz.*, electrons, positrons, protons, neutrons, and alpha particles. Since the alpha particle has an atomic mass of four and a positive charge of two, it is not considered to be one of the fundamental units. At least three of the remaining four particles are

needed to account for observed relationships. *The three particles now commonly accepted as unit particles of structure in the atoms of the chemical elements are the electron, the proton, and the neutron.* The neutron might be an electron-proton pair, and the proton might be a neutron-positron pair, but the mass, energy, and volume relationships do not justify either of these assumptions. It is presumed that the energy changes that occur during certain atomic disintegrations lead to the formation and emission of positrons, although they may not actually be present as structural units of the atoms.

The Nuclear Atom. In 1911, Rutherford proposed the following hypothesis: *All of the positive electricity and nearly all of the mass of the atom is concentrated in a very small nucleus, with enough electrons outside of this nucleus to equal the positive charge.* This hypothesis is supported by the deflection of alpha ray particles passing through thin metal films. A large proportion of the particles in an alpha ray beam pass through such a metal film placed in its path and fall upon a screen without significant change in direction, while others show large deflections. Consequently, rays are scattered over a wide area after passing through the metal film. The deflections are too great to be caused by single electrons or protons, but they are caused by atomic nuclei having large masses and electric charges. The small proportion of the particles suffering deflection indicates that the atomic nuclei are so small, and so far apart relative to their sizes, that many alpha particles pass directly through the metal film without coming near enough to an atomic nucleus to be affected.

Atomic Numbers. Rutherford calculated the nuclear charges of a number of atoms from the measured deflections of alpha particles passing through metal films, and concluded that the charge of the nucleus is equal to approximately one half of the atomic weight. A method for the exact determination of the nuclear charge was developed in 1913 by the British physicist, Moseley, who was killed at Gallipoli in 1915. Moseley determined the wave lengths of the X-rays produced through the use of different elements on the anticathode in an X-ray tube. He found that the X-rays produced by each of the elements are complex, and that the spectrum of each element contains certain characteristic lines. The lines of shortest wave length, *i.e.*, of highest frequency, constitute the K-series,

the only series shown characteristically by all of the elements. The wave lengths of the lines in a particular series are slightly shorter for elements of the higher atomic weights. Moseley found that the relation of these wave lengths for successive elements may be expressed in an arithmetical progression (Fig. 66), and that a number may be assigned to each of the elements, beginning with 1 for hydrogen and continuing regularly to 92 for uranium, which
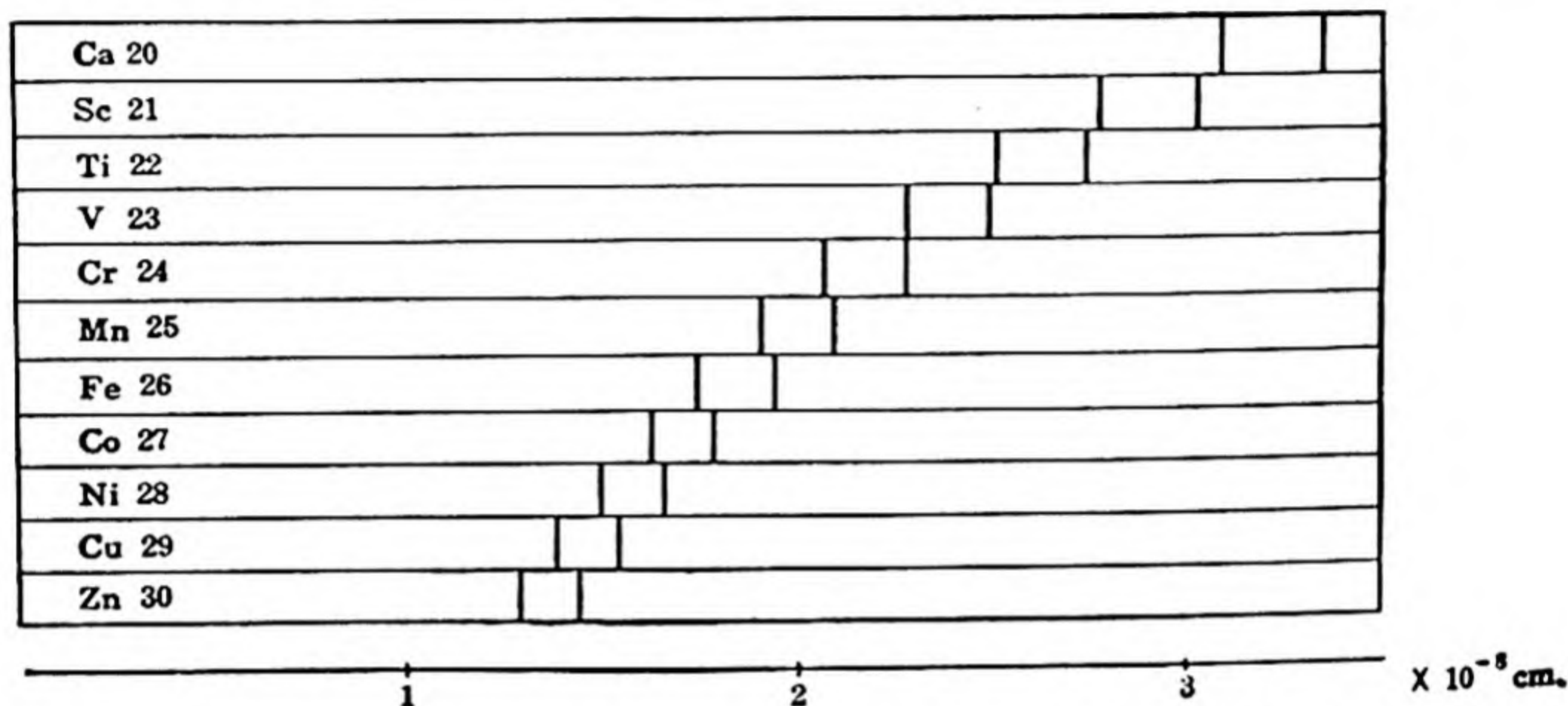
Fig. 66. *Wave-Lengths of K-Series X-Ray Lines.* (*Moseley*)

shows the position of that element in the series. These numbers are called *atomic numbers*. Moseley determined experimentally the atomic numbers of most of the elements in the list from sodium to gold. Chadwick has proved that *atomic numbers are equal to the nuclear charges of the respective atoms.* The atomic number is now considered the distinguishing feature of an element rather than the atomic weight.

The Atomic Nucleus. According to generally accepted theories dealing with atomic structure, the nucleus is a very small, compact, central part of an atom. It contains all of the protons and neutrons in the atom, and the mass of the atom depends on the numbers of protons and neutrons the nucleus contains.* The atomic number is the positive charge of the nucleus which, according to theory, is equal to the number of protons in the nucleus. Consequently, the number of neutrons in a particular atomic nucleus is equal to the

* The total weight of all of the electrons contained in even the most complex of the atoms is only a small fraction of one atomic weight unit, so that the weight of the nucleus is practically the entire weight of the atom.

difference between the atomic number and the atomic weight. The numbers of protons and neutrons in the atoms of the lower atomic numbers are nearly equal, but the relative number of neutrons becomes increasingly great in the order of higher atomic numbers. In the uranium atom, the number of neutrons is approximately one and one-half times the number of protons.

That the weights of complex nuclei are not integral multiples of the weights of single neutrons and protons has been explained by Harkins as due to the *packing effect, i.e.,* the loss of mass through the energy changes caused by the close packing of these particles in the atomic nucleus. Naturally occurring varieties of many of the elements are mixtures of two or more kinds of atoms having different masses but the same atomic number. The difference in mass is attributed to different numbers of neutrons in the atomic nucleus. Atomic weights determined experimentally are average weights that depend on the relative numbers of the different varieties of atoms in the mixture. Consequently, the atomic weights of many of the elements are not integral numbers.

Isotopes. Atoms of different atomic mass but the same atomic number are *isotopes. An element is a variety of matter composed of atoms having the same atomic number.* Aston has shown that isotopic varieties of elements may be separated, and the masses of the different
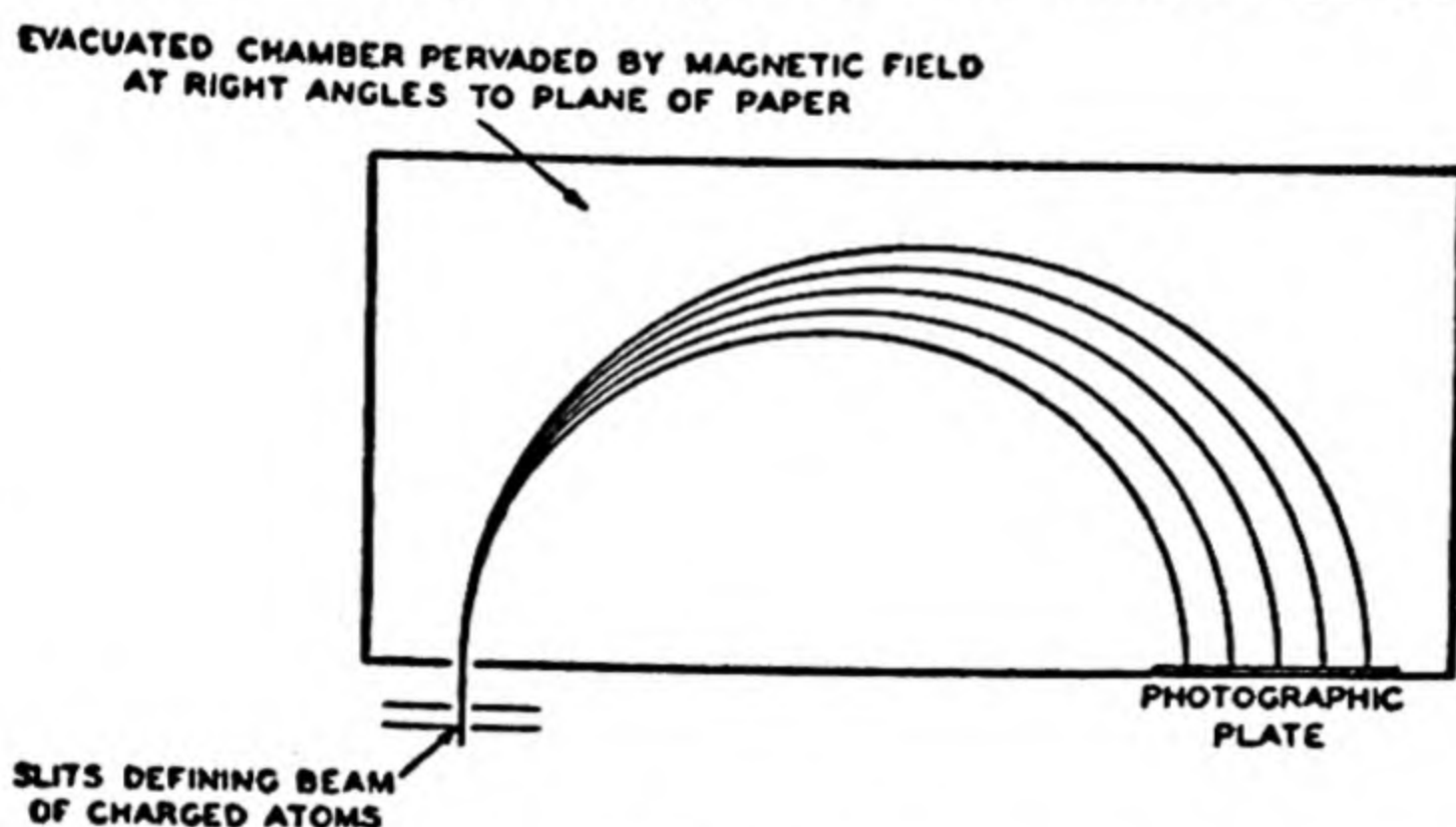
Fig. 67. *Illustrating the Separation of Isotopes.* (From Darrow, *The Renaissance of Physics*)

particles may be determined. The separation is effected by converting the atoms into positive ray particles, gas ions, which are then caused to pass through a magnetic field. The rays are deflected

to an extent that depends on the mass, velocity, and charge of the particle and the strength of the field. Particles having the same charge and velocity but different masses are deflected to different degrees as they pass through the same magnetic field. By the application of this principle, the rays are separated and may be allowed to fall on a photographic plate (Fig. 67), producing a spectrum. The relative masses of the atoms may be determined from measured deflections by reference to a standard. The apparatus is known as the *mass spectrograph*. It may be employed for the determination of exact atomic weights. In Table 18 stable isotopes of some of the familiar elements are listed, the most abundant isotope being represented in each instance by the first atomic weight.

TABLE 18. STABLE ISOTOPES OF SOME OF THE COMMON ELEMENTS

Element	Atomic Number	Atomic Weight	Isotopes
H	1	1.0080	1, 2
C	6	12.01	12, 13
N	7	14.008	14, 15
Mg	12	24.32	24, 25, 26
Cl	17	35.457	35, 37
Fe	26	55.84	56, 54, 57, 58
Cu	29	63.57	63, 65
Br	35	79.916	79, 81
Ag	47	107.88	107, 109
Cd	48	112.41	114, 106, 108, 110, 111, 112, 116
Sn	50	118.70	120, 112, 114, 115, 116, 117, 118, 119, 122, 124
Te	52	127.61	128, 130, 120, 122, 123, 124, 125, 126
Pb	82	207.21	208, 207, 204, 206
U	92	238.07	238, 235

The isotopes of an element have the same number of protons in the nucleus, but different numbers of neutrons. Thus, the atomic number of chlorine is 17, and its two isotopes have atomic weights of 35 and 37. Each of these atomic nuclei contains 17 protons, but according to the theory, the numbers of neutrons are 18 and 20, respectively. Ordinary chlorine is a mixture of these two isotopes in such proportions that the average value is 35.46, *i.e.*, the atomic weight determined by chemical methods.

The Electrons in the Atom. The atom of an uncombined element is electrically neutral in its normal state. Hence, it is evident that it contains equal numbers of electrons and protons. According

to the theory, all electrons in an atom are outside of the nucleus. The radius of the electron has been calculated to be approximately a fifty thousandth of the radius of the atom, although this ratio varies because some atoms are larger than others. The distances between the nucleus and the electrons are enormous relative to their sizes.

The chemical reactions of the elements are correlated with the relationships of the electrons. The atomic ratio in which elements react with one another is definite and is usually a ratio of small integers. Hence, it is necessary to conclude that the electrons in an atom do not all bear the same relation to the atomic nucleus, except in the hydrogen and helium atoms. All but six elements show varying degrees of chemical activity. These inert elements together with their atomic numbers are: helium, 2; neon, 10; argon, 18; krypton, 36; xenon, 54; and radon, 86. Since these elements are inert, it is evident that the number of electrons they contain impart chemical stability to the atom. Other elements enter into chemical reactions under appropriate conditions because their atoms do not possess structural stability. It is, therefore, assumed that certain arrangements of the electrons give the atoms stability while other arrangements do not.

Electron Distribution. Chemical evidence based on the periodicity of the elements lends support to the conclusion that the properties of the elements are due to the distribution of their electrons into specific series or periods. The electrons in these different series possess different amounts of energy. The energy level of the electrons depends on their energy content. According to this mechanical picture, electrons are moving as discrete particles in different paths around the nucleus of the atom, and the number of electrons in each class of orbits is limited. These paths of the electrons in a particular series may be thought of as constituting an energy region or shell. It is customary to speak of classifying the electrons into different shells. In terms of this model, the electron shells of the inert gases contain the maximum number of electrons in each class of orbits. The theory assumes that the first shell is complete with two electrons and the second, with eight. The hydrogen atom contains a single electron in a particular shell, and the helium atom contains two in this shell. These electrons are at

the lowest energy level in the atoms. The atoms of the next eight elements (in the order of their atomic numbers) contain, successively, one to eight electrons in a second shell at higher energy levels. The third electron shell is likewise complete with eight electrons, so long as it is the outermost shell of the atom. It must be assumed, however, that this shell may contain additional numbers of electrons after a fourth shell containing two electrons has appeared. The third shell is finally complete with eighteen electrons. Similar assumptions are made regarding subsequent electron shells. The maximum number of electrons in any shell is in the atom of the inert gas in that period, Table 19

TABLE 19. ARRANGEMENT OF ELECTRONS IN THE INERT GASES

Element	Atomic Number	First Shell	Second Shell	Third Shell	Fourth Shell	Fifth Shell	Sixth Shell
Helium	2	2					
Neon	10	2	8				
Argon	18	2	8	8			
Krypton	36	2	8	18	8		
Xenon	54	2	8	18	18	8	
Radon	86	2	8	18	32	18	8

The electron distribution in the atoms of the elements through the first long period is shown in Table 20.

The assumption that the electrons may be at different energy levels in atoms is supported by a consideration of X-ray spectra. The lines in the K-series are attributed to the electrons in the lowest energy region, the electron shell of the helium structure. These lines are shown characteristically by all of the remaining elements, with a shift to shorter wave lengths as the atomic numbers increase. Additional lines appear in the X-ray spectra corresponding to additional electron shells.

The Direct Union of the Elements. In accord with the electron distribution discussed in the preceding paragraph, the reactions of elementary substances involve a redistribution of electrons in their atoms. During these changes, the atoms tend to acquire the electron structure of an inert gas, although there are many reactions in which they do not actually reach such a structure. There are three changes by which an atom may approach or reach the electronic structure of an inert gas. *It may lose electrons*

TABLE 20. ELECTRON DISTRIBUTION IN THE ATOMS OF
ELEMENTS 1–36

Element	Atomic Number	First Shell	Second Shell	Third Shell	Fourth Shell
H	1	1			
He	2	2			
Li	3	2	1		
Be	4	2	2		
B	5	2	3		
C	6	2	4		
N	7	2	5		
O	8	2	6		
F	9	2	7		
Ne	10	2	8		
Na	11	2	8	1	
Mg	12	2	8	2	
Al	13	2	8	3	
Si	14	2	8	4	
P	15	2	8	5	
S	16	2	8	6	
Cl	17	2	8	7	
A	18	2	8	8	
K	19	2	8	8	1
Ca	20	2	8	8	2
Sc	21	2	8	9	2
Ti	22	2	8	10	2
V	23	2	8	11	2
Cr	24	2	8	12	2
Mn	25	2	8	13	2
Fe	26	2	8	14	2
Co	27	2	8	15	2
Ni	28	2	8	16	2
Cu	29	2	8	18	1
Zn	30	2	8	18	2
Ga	31	2	8	18	3
Ge	32	2	8	18	4
As	33	2	8	18	5
Se	34	2	8	18	6
Br	35	2	8	18	7
Kr	36	2	8	18	8

from its outer shell, it may gain additional electrons, or atoms may share electrons. The electrons in an incomplete outer shell of an atom are called *valence electrons*, because the reacting ratio is dependent on their number.

The electrons lost in one process are gained in another. Hence, reactions of elements involving gain or loss of electrons are due to *electron transfer*. The electron relations in such reactions may be represented in a simple and useful manner according to a system.

proposed by G. N. Lewis. The symbol is allowed to represent all of the atom, except the electrons in the valence shell. This part of the atom is called the *kernel*. Dots are now written about each symbol to represent the valence electrons. Sodium has the atomic number 11, and the electron distribution in its atom is 2, 8, 1. Similarly, chlorine has the atomic number 17 and the electron distribution 2, 8, 7. According to this plan for electronic notation, Na· represents the sodium atom and : $\overset{..}{\underset{..}{Cl}}$ · the chlorine atom. The equation representing the reaction of sodium atoms with chlorine atoms may be written:

$$\text{Na} \cdot \; + \; : \overset{..}{\underset{..}{\text{Cl}}} \cdot \; \longrightarrow \; (\text{Na})^+ \; + \; (: \overset{..}{\underset{..}{\text{Cl}}} :)^-$$
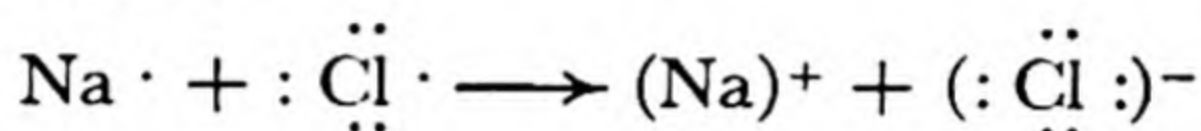
Each sodium atom acquires the electron configuration of neon by the loss of one electron and is changed into an ion. Simultaneously, each chlorine atom acquires the configuration of argon by the gain of one electron and is changed into a chloride ion. Magnesium reacts with sulfur, two electrons being transferred from a magnesium atom to a sulfur atom.

$$\text{Mg} : \; + \; \overset{..}{\underset{..}{\text{S}}} : \; \longrightarrow \; (\text{Mg})^{++} \; + \; (: \overset{..}{\underset{..}{\text{S}}} :)^{--}$$
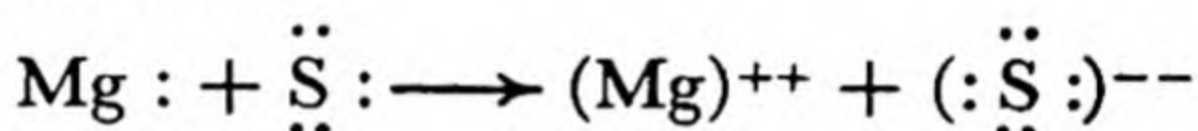
Molecules of some of the elementary gases contain two atoms. It is assumed that a pair of electrons is held jointly by both atoms in such molecules. Pairs of electrons, which are inherent structural parts of two atoms, are known as *shared electrons*. The electronic formula of chlorine is written in the following equation representing the reaction of sodium with molecular chlorine.

$$2\,\text{Na} \cdot \; + \; : \overset{..}{\underset{..}{\text{Cl}}} : \overset{..}{\underset{..}{\text{Cl}}} : \; \longrightarrow \; 2\,(\text{Na})^+ \; + \; 2\,(: \overset{..}{\underset{..}{\text{Cl}}} :)^-$$
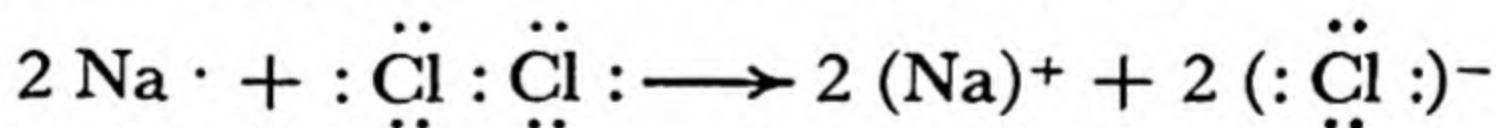
Electrons may be shared by dissimilar atoms in the molecules of compound products.

$$\text{H} : \text{H} \; + \; : \overset{..}{\underset{..}{\text{Cl}}} : \overset{..}{\underset{..}{\text{Cl}}} : \; \longrightarrow \; 2\,(\text{H} : \overset{..}{\underset{..}{\text{Cl}}} :)$$
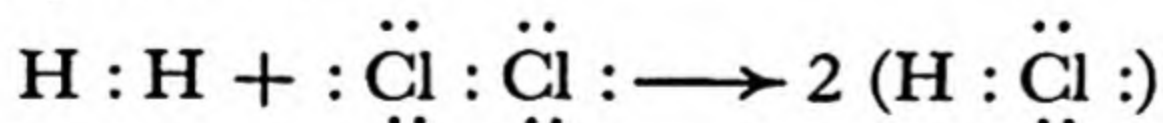
Both of the electrons in the pair may originate from the same atom. In the reaction of sulfur with oxygen to form sulfur dioxide, it is supposed that each of the electron pairs is from the sulfur atom.

$$: \overset{..}{\underset{..}{\text{S}}} : \; + \; : \overset{..}{\underset{.}{\text{O}}} : \overset{..}{\underset{.}{\text{O}}} : \; \longrightarrow \; : \overset{..}{\underset{.}{\text{O}}} : \overset{..}{\text{S}} : \overset{..}{\underset{..}{\text{O}}} :$$
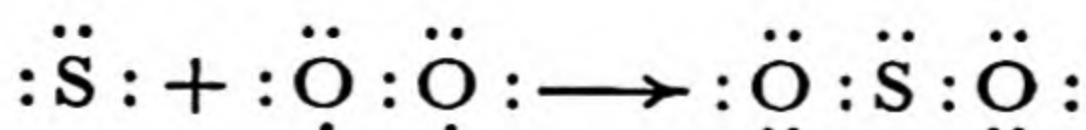
The direct union of two elementary substances involves either a transfer of electrons from one variety of atom to another, or the sharing of electrons by atoms of the two elements.

Electronic Nature of Valence. An element's valence is defined as the number of hydrogen atoms its atom will combine with or displace. Each hydrogen atom may furnish one electron in combination reactions, and each hydrogen ion must gain one electron in displacement reactions. Hence, the combining capacity of an atom is measured in terms of electrons. Uncombined elements are in a zero valence state. Two types of valence bonds result from the electronic changes that occur during the union of elementary substances, *viz.*, electrovalence and covalence.

Electrovalence. The atoms of uncombined elements are electrically neutral. Consequently, they are changed into positive ions by the loss of electrons and into negative ions by an electron gain. *Ions are atoms or radicals bearing electric charges.* Oppositely charged particles exert forces of attraction on one another. In the solid state the forces of attraction are great enough to hold the ions in fixed positions in crystals, and such compounds are *ionic substances*. *The positive electrovalence of an ion* is equal to the number of electrons required to convert it into a neutral atom. *The negative electrovalence of an ion* is equal to the number of electrons that must be removed to form a neutral product. Elements composed of atoms containing only one or two valence electrons usually form positive ions by giving up electrons during their reactions. The maximum number of electrons an atom may give up is the number in the valence shell, increased in some instances by one or more electrons from an incomplete inner shell. Elements composed of atoms having only one or two electrons less than the next higher inert gas readily gain electrons to form negative ions. The maximum number of electrons an atom may gain is the number required to complete the valence shell.

Covalence. Many reactions involve electron-sharing with the formation of molecular products. Valence due to the sharing of electrons is known as covalence. In the ordinary covalent bond, each atom contributes one electron to the pair. *One unit of covalency is due to a bond made up of one electron pair.* The covalency of each atom of hydrogen and chlorine in hydrogen chloride is one. The

covalency of oxygen is two and of carbon four in many of their compounds. In the following electronic formulas, the valence electrons are represented by dots, according to the plan discussed in a preceding paragraph.

$$
\begin{array}{cccc}
\overset{\cdot\cdot}{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : & \quad : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : & \quad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : : C : : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} & \quad H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : \\
H & : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : & & \\
H_2O & CCl_4 & CO_2 & HCl
\end{array}
$$
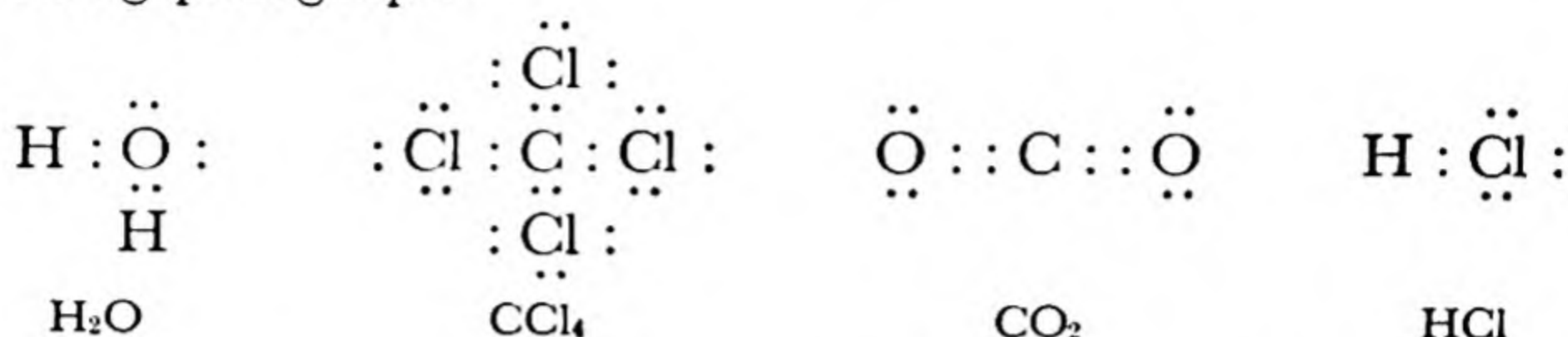
In some compounds, the electron pairs appear to be held equally by both of the atoms involved, and the molecules are symmetrical. Such molecules are *nonpolar*. Carbon tetrachloride and molecular chlorine are composed of nonpolar molecules. In certain other substances, the electron pairs constituting the bond appear to be held more strongly by one of the atoms than by the other. Molecules of these substances are unsymmetrical since one part of the molecule is negative toward the other part, *i.e.*, the centers of the negative and positive charge do not coincide. Such substances are *polar*. Water, hydrogen chloride, and ammonia are familiar substances composed of polar molecules. The polarity of a molecule depends on the degree of separation of the positive and negative charges. Compounds composed of polar molecules differ in many of their properties from those that are nonpolar. The effects of polarity are particularly important in the liquid state when the molecules are close together and yet are free to move with respect to one another.

The special type of covalent bond, in which both of the electrons of the pair originate in the same atom, is called a *coordinate bond*. This is the nature of the bond in sulfur dioxide, shown in a preceding paragraph. The coordinate bond is common among the nonmetal oxides and among complex radicals composed of nonmetal and oxygen atoms.

Oxidation Numbers. The valence is equal to the electrical charge of the ions *in ionic compounds*. The sodium ion has a positive electrovalence of one, the chloride ion, a negative electrovalence of one. The loss of an electron by an atom or ion causes an increase in the positive charge, and the gain of an electron causes a decrease. An increase in the positive valence of an element is defined as

oxidation and a decrease, as reduction. Therefore, in electrovalent compounds, oxidation is the loss of electrons, and reduction the gain of electrons. *Oxidation-reduction* is the transfer of electrons from one atom or ion to another.

In molecular compounds, however, electrons are not transferred but are shared, and no free electrically charged particles are present. It is assumed that electron pairs are displaced toward one of the atoms in polar molecules, but it must also be assumed that they are shared equally in nonpolar molecules. Nevertheless, arbitrary assumptions are made by assigning positive and negative numbers to the elements in molecular compounds. These numbers, called *oxidation numbers*, are assigned through a consideration of the general behavior of the elements. In general, however, the oxidation number of oxygen in most of its compounds is 2− and of hydrogen 1+, except in the metal hydrides. Chlorine atoms exhibit greater activity in gaining electrons than in losing them. Hence, the oxidation number 1− is assigned to chlorine in most of its binary compounds, except with oxygen. A series of oxidation numbers for the elements may be derived on the basis of a few arbitrarily assigned numbers and the rule that the sum of the positive oxidation numbers of the atoms in a molecule is equal to the sum of the negative numbers. Thus, phosphorus trichloride, PCl_3, is a molecular substance in which the bonding is of the covalent type. The oxidation number of chlorine is 1−, and the three atoms of chlorine give a total of 3−. Hence, the oxidation number of phosphorus is 3+ in this compound. A similar procedure is employed in calculating the oxidation numbers of the elements in more complex compounds. In potassium chlorate, $KClO_3$, the oxidation number of potassium is 1+ and of each oxygen, 2− or a total of 6− for the three atoms of oxygen. Therefore, the oxidation number of chlorine in this compound is 5+, and the total of the positive numbers is also 6.

Some elements may have more than one oxidation number, depending on experimental conditions. Thus, chlorine gains electrons in its reaction with the metals and has an electrovalence of 1− in the resulting salts. With hydrogen, electrons are shared, and chlorine has a covalent oxidation number of 1− in hydrogen chloride. Chlorine may yield products in the oxidation states represented by the numbers 1 +, 3 +, and 7 +, in addition to the

5 + state, and the uncombined element is in a 0 state of oxidation. The change in oxidation numbers involving covalent bonds is oxidation-reduction, but the electronic change usually requires the presence of one or more substances in addition to those actually undergoing oxidation and reduction.

Periodicity and Atomic Numbers. The arrangement of the elements in the order of their atomic numbers places them in the same order as the arrangement according to atomic weights, except that it corrects the discrepancies previously noted in the positions of argon and potassium, cobalt and nickel, and tellurium and iodine. Since the atomic numbers range from hydrogen 1 to uranium 92, there should be ninety-two naturally occurring elements. The chemical reactions of the elements depend on the number of planetary electrons and, consequently, on the atomic numbers. **The Periodic Law may be restated: The properties of the chemical elements are periodic functions of their atomic numbers.** The repetition in properties is due to a repetition of the essential features of the structure of the atoms of the elements. The elements in each main group have the same number of valence electrons, and the kernels of the atoms are made up of complete electron shells. In Table 21, the periodic classification of the elements is arranged in the same form as in Table 15, except that atomic numbers are listed instead of atomic weights. The group number indicates the number of valence electrons in the atoms of the elements in the main groups, with the exception of Group VIII. The elements listed to the right of the heavy line are nonmetals.

The differences in the properties of the elements in the sub-groups are attributed to the fact that the kernels of the atoms are not made up of complete and stable electron shells. Consequently, electrons in the outer shell, and also some of those in an incomplete inner shell, may contribute to the chemical behavior of these elements.

The activity relationships in a group of active metals, such as the alkali metals, is satisfactorily explained in terms of atomic structure. The activities of these metals depend on the ease with which their atoms give up electrons to form positive ions. In most of the reactions of the alkali metals, the elements of high atomic numbers are more active than those of low atomic numbers, al-

TABLE 21. PERIODIC CLASSIFICATION OF THE ELEMENTS BASED ON ATOMIC NUMBERS

Period ↓ \ Group→	I	II	III-B	IV-B	V-B	VI-B	VII-B	VIII-B			I-B	II-B	III	IV	V	VI	VII	VIII
I 2 Elements	H 1																	He 2
II 8 Elements	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
III 8 Elements	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	A 18
IV 18 Elements	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
V 18 Elements	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
VI 32 Elements	Cs 55	Ba 56	57 ª 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	Rn 86
VII 6 Elements	— 87	Ra 88	Ac 89	Th 90	Pa 91	U 92												

— Transition Elements —

ª The elements with atomic numbers 57–71 are: La, 57; Ce, 58; Pr, 59; Nd, 60; Il, 61; Sm, 62; Eu, 63; Gd, 64; Tb, 65; Dy, 66; Ho, 67; Er, 68; Tm, 69; Yb, 70; Lu, 71. These elements comprise the rare earths. They contain the same number of valence electrons, and their atoms differ in the number of electrons in the fourth shell.

though lithium, the first member of the group, shows irregular behavior in this respect.

The greater activity in the loss of electrons by the larger and more complex atoms may be understood by a consideration of the diagrams in Fig. 68. The small dot at the center represents the positive nucleus containing protons and neutrons. The concentric circles represent the electron shells. The force holding an electron
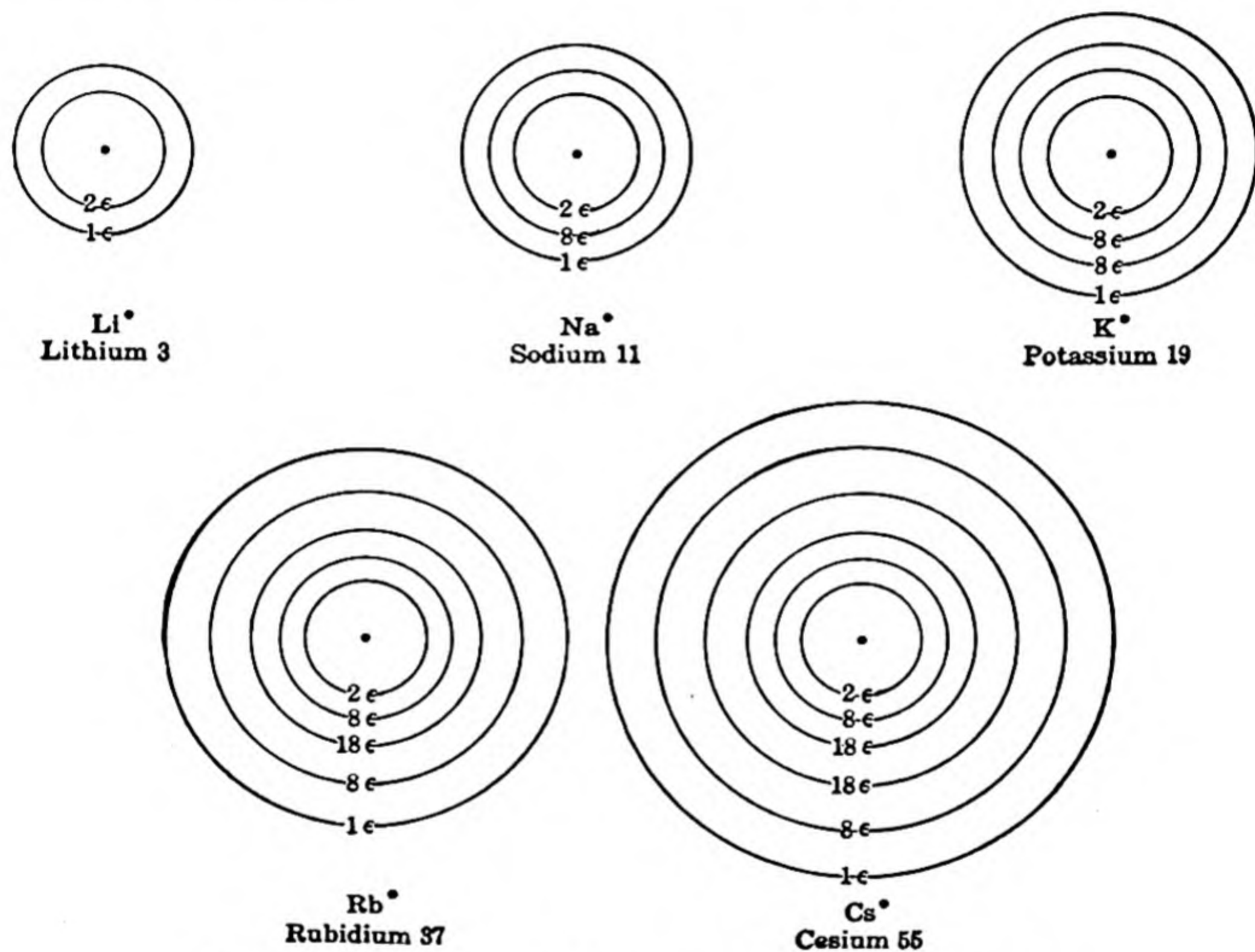
Fig. 68. *Diagrams of the Atoms of the Alkali Metals*

in its valence shell depends on the charge and size of the kernel of the atom, decreasing as the atoms grow larger. The atomic kernel, all of the atom except the valence electron, has the same charge in each atom in this group, but the ions resulting from the loss of the valence electron are progressively larger in the order of increasing atomic numbers. The electrons in the first shell are bound more strongly to the nucleus than the other electrons, because they are within the shells of the remaining electrons and are in the field of the nuclear charge. Those in the second shell are further from the atomic nucleus and the force of its attraction by

the nucleus is less. The valence electron in each alkali metal is held less firmly than in the corresponding atom of the preceding period.

The activity relationships in a group of active nonmetals are in the opposite order to the alkali metals. The activities of the halogens depend on the ease with which they gain electrons to form negative ions. The attraction of the nucleus for an electron in a particular energy shell depends on the charge of the nucleus and the size of the atom. The nuclear charge is greater in the atoms of high atomic number than in those of low atomic number but the atoms are much larger. The electron required to complete the valence shell of the halogen is attracted much less strongly in the larger atoms than in the smaller ones. In groups of nonmetals, the activity commonly decreases with increasing atomic number.

Nuclear Transformations. The nuclei of some of the naturally occurring elements are unstable, and others may be made unstable by bombarding them with different high energy particles such as protons, neutrons, deuterons, and alpha particles. If the ratio between the numbers of neutrons and protons is either smaller or greater than the range of stable ratios for any individual atom, the nucleus is so unstable that it undergoes a change in structure, with the emission of different types of radiation. The evaporation of these simple particles from the highly energetic nuclei causes the system to lose enough energy to become stable.

In some atomic nuclei, the number of neutrons is too great to give a ratio to the number of protons that falls within the stable limit. The excess of neutrons over protons may be reduced by the emission of neutrons and by the transformation of neutrons into protons with emission of electrons. The latter change, the emission of beta ray particles, is the change commonly observed among the natural radioactive elements by which the excess of neutrons in the nucleus is reduced.

In the other type of unstable atomic nuclei, the number of neutrons is too small to give a ratio to the number of protons within the stable limit. The excessive charge of the nucleus may be reduced by the emission of alpha rays, the emission of protons, the emission of positrons, and by the capture of electrons. Among the natural radioactive elements of high atomic weight, the emission of alpha

rays is the common change by which the charge of the nucleus of the atom is decreased.

Artificial Radioactivity. A number of the elements composed of stable atoms exhibit radioactivity when bombarded by high energy particles. Radioactivity produced in this manner, known as artificial radioactivity, was discovered in 1933 by Mme. Irene Curie Joliot and M. Frederic Joliot, her husband. They found that the bombardment of boron by alpha rays produced an unstable isotope of nitrogen with an atomic mass of 13. Neutrons are given out in this change. Nuclear changes may be represented by equations in which a subscript preceding the symbol represents the atomic number and a following superscript the atomic mass of the particular isotope involved. The neutron is represented by n, the positron by p and the proton by H.

$$_5B^{10} + {_2}He^4 \longrightarrow {_7}N^{13} + {_0}n^1$$
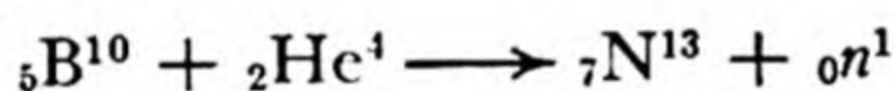
This isotopic variety of nitrogen is unstable, decomposing with the emission of a positron and the formation of an isotope of carbon.

$$_7N^{13} \longrightarrow {_6}C^{13} + {_1}p^0$$

Elements that exhibit artificial radioactivity are called *radioelements*. The number of radioelements now known is about 370. The majority of the elements have been obtained in several radioactive isotopes.

Since the alpha particle has a positive charge of two units, it is repelled by the positively charged atomic nuclei. Hence, alpha particles must possess high kinetic energy to overcome the potential barrier and enter the atomic nucleus. Alpha particles are discharged from the atoms of radioactive elements with high enough velocity to cause a number of nuclear changes. Some of the lighter atomic nuclei undergo transmutation by the capture of alpha particles, with the formation of unstable nuclei that decompose to give out protons. The transmutation of nitrogen first observed by Rutherford in 1919 may be represented by the equation:

$$_7N^{14} + {_2}He^4 \longrightarrow {_9}F^{18} \longrightarrow {_8}O^{17} + {_1}H^1$$
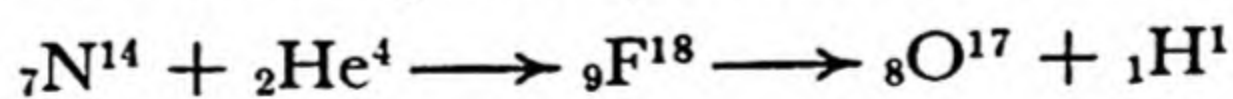
The loss of a proton reduces the charge of the nucleus and improves the neutron-proton ratio so as to give a stable product. In other instances, the unstable atomic nucleus formed by the capture of

an alpha particle may have too high a neutron-proton ratio and may decompose with the emission of a neutron.

$$_3Li^7 + {}_2He^4 \longrightarrow {}_5B^{11} \longrightarrow {}_5B^{10} + {}_0n^1$$
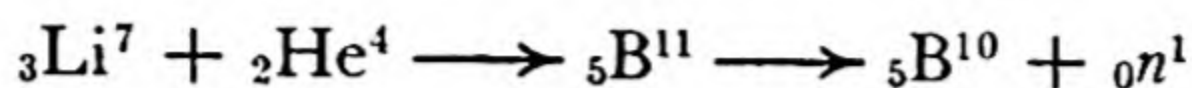
Experimental techniques have been developed whereby charged particles, such as deuterons and protons, may be accelerated so that they have sufficient kinetic energy to overcome the potential barrier and react with atomic nuclei. The cyclotron invented by Lawrence is a device by which such particles may be accelerated
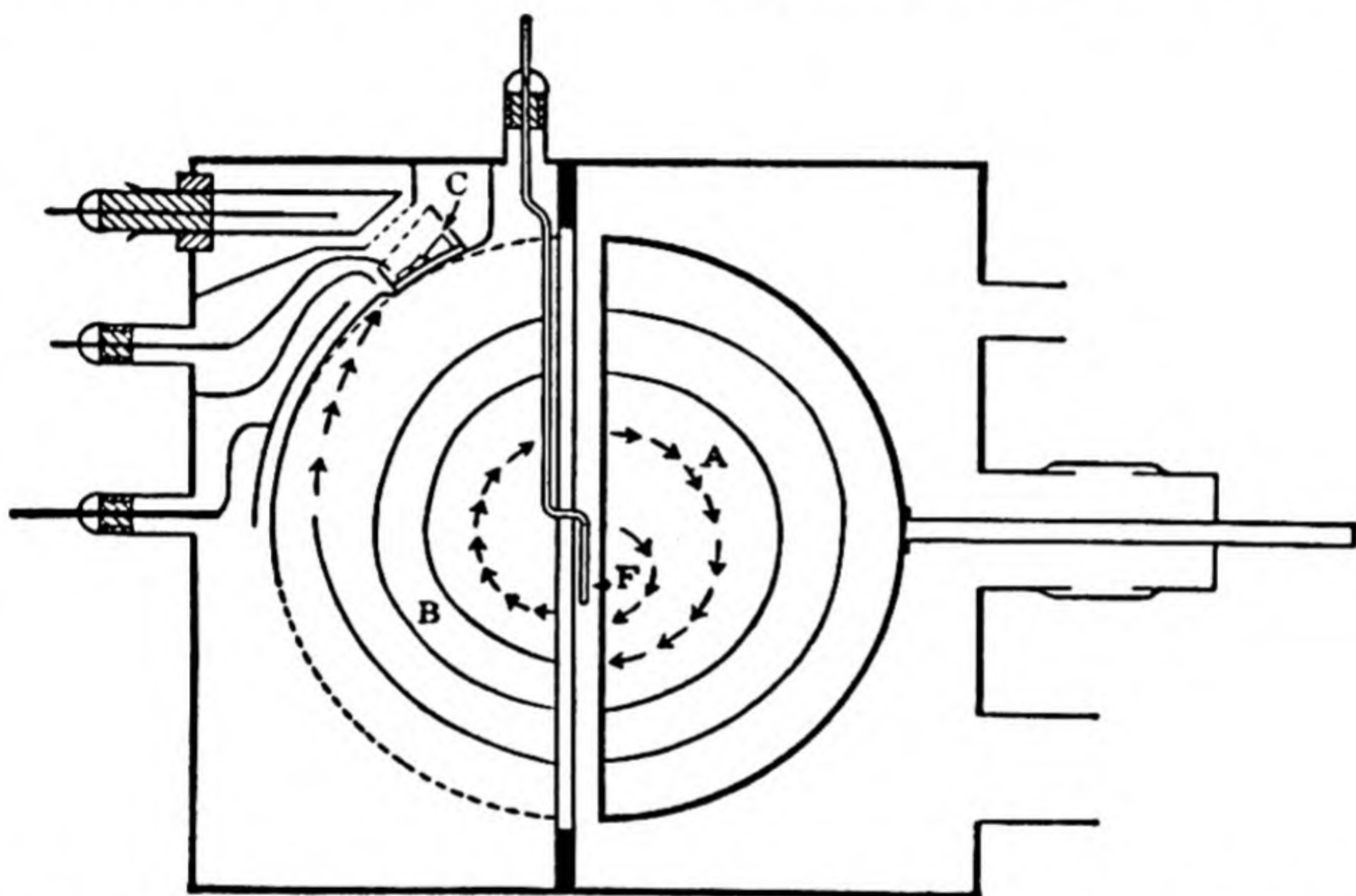
Fig. 69. The Cyclotron (From Darrow, The Renaissance of Physics)

in multiple stages. The cyclotron vacuum chamber contains two hollow semicircular electrodes coupled to a powerful source of current, using a vacuum-tube oscillator so that the polarity is reversed at proper intervals. The tungsten filament at the center of the chamber furnishes electrons to cause the ionization of the gas in the chamber. This vacuum chamber is placed between the poles of a powerful electromagnet. Gas ions formed at the filament F (Fig. 69) are drawn into the electrode A, and describe a semicircular path under the influence of the magnetic field at right angles to the plane of motion. As the gas ions complete the semicircle A, the charge of the electrodes is reversed, and the ions are accelerated as they cross the gap and enter the electrode B.

Since the ions are now moving faster, they have greater kinetic energy and follow the arc of a larger semicircle. An added impulse is given in the same manner each time the ions cross the gap from one region to the other. The particles follow a spiral path as their energies increase, until they strike the substance under investigation at C. The kinetic energy of the fast-moving particles is conveniently expressed in electron volts. *The electron volt* is so defined that an electron traveling through a vacuum between two points, which differ in potential by one million volts, acquires an energy of one million electron volts. Protons and deuterons may be accelerated in the chamber so as to acquire energies in excess of 6 million electron volts.

A number of transmutations are caused by the fast-moving *protons and deuterons*. The quantities of material produced by this procedure are small, because only a relatively small proportion of the high velocity particles actually strike an atomic nucleus, causing transmutation. The lithium nucleus of atomic weight 7 yields alpha particles when bombarded with protons.

$$_3Li^7 + {_1}H^1 \longrightarrow 2\ {_2}He^4$$
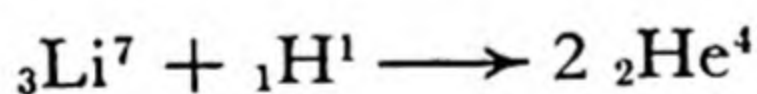
There are several atomic nuclei that emit neutrons when they are bombarded with deuterons.

$$_3Li^7 + {_1}H^2 \longrightarrow 2\ {_2}He^4 + {_0}n^1$$
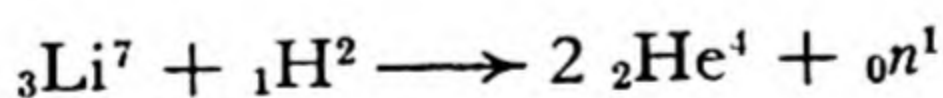
The neutron cannot be accelerated in an electromagnetic field, because it has no charge. However, neutrons produced by the bombardment of beryllium with alpha particles and by the action of deuterons on deuterium have large kinetic energies and readily penetrate atomic nuclei. The energy of the nucleus is greatly increased by the absorption of a neutron, because a portion of the mass of the neutron is converted into energy. This produces a great heating effect on the nucleus and causes the evaporation of small mass-energy particles, thus releasing some of the surplus energy.

$$_{11}Na^{23} + {_0}n^1 \longrightarrow {_{11}}Na^{24}$$
$$_{13}Al^{27} + {_0}n^1 \longrightarrow {_{11}}Na^{24} + {_2}He^4$$
$$_{13}Al^{27} + {_0}n^1 \longrightarrow {_{12}}Mg^{27} + {_1}H^1$$
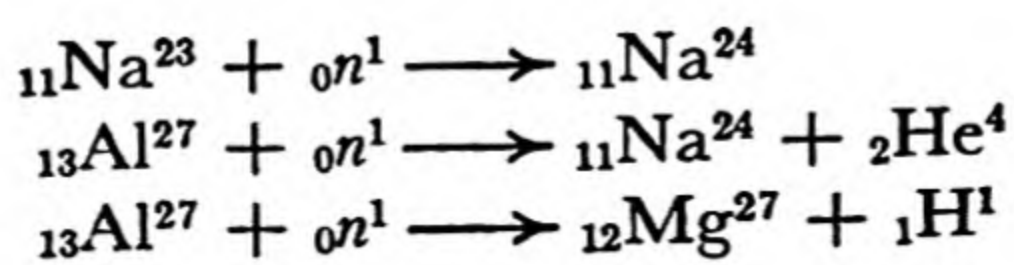
The nuclei formed in these reactions are unstable and decompose, reducing the ratio of neutrons to protons by the emission of electrons. Consequently, they exhibit beta ray activity.

$$_{11}Na^{24} \longrightarrow {}_{12}Mg^{24} + \epsilon$$
$$_{12}Mg^{27} \longrightarrow {}_{13}Al^{27} + \epsilon$$
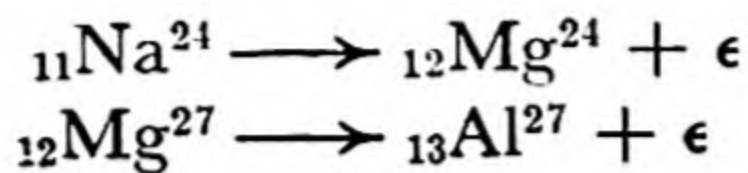
EXERCISES

1. Name the three particles which are regarded as fundamental units of atomic structure. What is the mass and electrical charge of each particle?
2. What are radioactive elements? What is the source of the radiations which they emit?
3. What is meant by transmutation of an element?
4. How is the complexity of atoms indicated by (a) transmutation of elements? (b) the existence of isotopes? (c) the formation of ions?
5. How may minute electrically charged particles be detected?
6. Give evidence to support the assumption that atoms have a nuclear structure.
7. What is the atomic number of an element?
8. What is the evidence that the electrons in an atom are at relatively great distances from the nucleus?
9. What is an electron shell?
10. In making a model of an atom what justification is there for the distribution of the electrons into shells?
11. What is the kernel of an atom?
12. What electronic changes may occur during the reactions of the elements?
13. What three types of valence result from the electronic changes that accompany the reactions of the elementary substances? Define, and give an example of each.
14. Write electronic formulas to represent the following compounds: (a) lithium fluoride and potassium bromide; (b) calcium chloride and calcium sulfide; (c) silicon dioxide and phosphorus pentoxide.
15. Define oxidation-reduction in terms of electronic changes, and illustrate by suitable examples.
16. What is an ionic compound? a nonpolar compound? a polar compound?
17. Show how the assumptions dealing with the structure of the atoms account for the following: (a) the periodic repetition in the properties of the elements; (b) the changes in the properties of the elements in a period; (c) the similarities shown by the elements in a family; (d) the differences in the activities of the elements in a family; (e) the inverted order of tellurium and iodine; (f) the existence of isotopes; (g) the divisibility of atoms; (h) the constancy of the reacting proportions of the elements.

SUPPLEMENTARY READINGS

Darrow, K. K., *The Renaissance of Physics*, The Macmillan Company, New York, 1936.

Millikan, R. A., *Electrons* (+ *and* −), *Protons, Photons, Neutrons, and Cosmic Rays*, University of Chicago Press, Chicago, 1935.

Briscoe, H. T., *Structure and Properties of Matter*, McGraw-Hill Book Company, Inc., New York, 1935.

Rutherford, E. R., J. Chadwick, and C. D. Ellis, *Radiations from Radioactive Substances*, Cambridge University Press, London, 1930.

Lewis, G. N., *Valence and the Structure of Atoms and Molecules*, The Chemical Catalog Company, Inc., New York, 1923.

Sidgwick, N. V., *The Electronic Theory of Valency*, Oxford University Press, London, 1932.

Aston, F. W., *Mass Spectra and Isotopes*, Edward Arnold & Co., London, 1933.

Rutherford, E. R., *The Newer Alchemy*, The Macmillan Company, New York, 1937.

Curie, Eve, *Madame Curie*, Doubleday, Doran & Company, Inc., New York, 1937.

Darrow, K. K., "Nuclear Fission," *The Bell System Technical Journal* **19**, 267 (1940).

Ridenour, L. N., and D. M. Yost, "Artificial Radioactivity," *Chemical Reviews* **18**, 457 (1936).

Chapter 14

IONIZATION

The effects of different solutes on certain properties of the solvent have been discussed in Chapter 7, page 114, and the fact that many solutes cause regular effects on the vapor pressure and related properties has been emphasized. These regular effects are approximately proportional to the mole fraction of the solute in the ideal solution, but corrections are required in many solutions, especially if the concentration of the solute is high. However, solutions of salts, acids, and basic hydroxides cause very irregular effects. Investigating the properties of the solutions of these three classes of compounds has led to important theories concerning the nature of the particles in aqueous solutions.

Vapor Pressure Effects Caused by Salts, Acids, and Basic Hydroxides. Experimental measurements show that salts, acids, and basic hydroxides in aqueous solution cause greater effects on the vapor pressure, freezing point, and boiling point of water than can be accounted for by the molal concentration of the solute. In a 0.1 molal solution of common salt, the freezing point depression is found to be 0.343°. This effect is approximately 1.85 times the effect in 0.1 molal solutions of solutes which become dispersed into molecules. The effects caused by hydrochloric acid and by sodium hydroxide are similar. Some solutes produce an effect greater than double, but less than triple that caused by molecular dispersions. From an investigation of a large number of substances, two conclusions may be drawn, *viz.*, the effects on the physical constants of water, caused by salts, acids, and basic hydroxides, are greater than proportional to the molal concentration, and these effects approach as a limit an integral multiple of the molecular effect. These effects depend on the relative numbers of solute and solvent particles. Common salt in one molal solution appears to furnish nearly twice as many solute particles as a mole of dextrose.

213

Salts, acids, and basic hydroxides yield a greater number of particles per mole in aqueous solution than substances that become dispersed into molecules. The concentration of the solute particles seems to be less than an integral multiple of the molecular concentration.

Two explanations of these abnormally great effects may be suggested. One may assume that a portion of the solute is in a molecular state of dispersion, while the remainder has become dissociated into smaller particles. Thus, if 95 per cent of a solute were in the molecular state and 5 per cent were broken up to give two particles for each molecule, the total number of particles furnished by the solute would be 1.05 times the number of molecules put into solution. A second assumption is that all of the solute is broken up into particles smaller than molecules and that the particles actually present suffer interferences that diminish their effect. The interferences in the sodium chloride solution mentioned above produce the same effect as though 15 per cent of the solute were in a molecular state. The apparent number of free particles of the solute is 1.85 times the number of molecules in one mole, although the actual number of solute particles is assumed to be twice this number.

Chemical Reactions of Solutions of Salts, Acids, and Basic Hydroxides. Soluble chlorides of metals react with solutions of silver nitrate to form a slightly soluble product, silver chloride. Certain other chlorine compounds, such as carbon tetrachloride and potassium chlorate, do not yield a precipitate with silver nitrate. These results show that chlorine in the metal chlorides in solution differs from the nonmetal chlorides and chlorates. Similarly, all acidic solutions have the common property of causing blue litmus to turn red and of reacting with active metals. Likewise, solutions of the soluble metal hydroxides cause phenolphthalein to turn red. The common properties shown by each of these classes of substances are logically attributed to a particular component. Obviously, such common, components are not molecules of the solute. The inference drawn from such observations is that a number of compounds may dissociate so as to yield the same component. Thus, the soluble metal chlorides yield the chloride radical; the acids yield the hydrogen radical; and soluble metal hydroxides

yield the hydroxide radical. This inference agrees completely with the conclusion stated in the preceding paragraph that the number of particles in such solutions is greater than in a molecular dispersion.

Electric Charges of Ions. It is evident that the particles in an aqueous solution of sodium chloride are not atoms of sodium and chlorine, because they do not have the properties of atoms. Solutions of the substances, which cause greater effects on vapor pressure and freezing and boiling points of water than accounted for by the molal concentration, are conductors of electric current. These substances are called *electrolytes*. Substances which do not yield conducting solutions are *nonelectrolytes*. During the passage of a direct current of electricity through a solution of an electrolyte, particles of one variety travel toward the anode, the positive electrode, and particles of the other variety toward the cathode, the negative electrode. (Fig. 70.) The attraction of these particles to the respective electrodes indicates that they are electrically
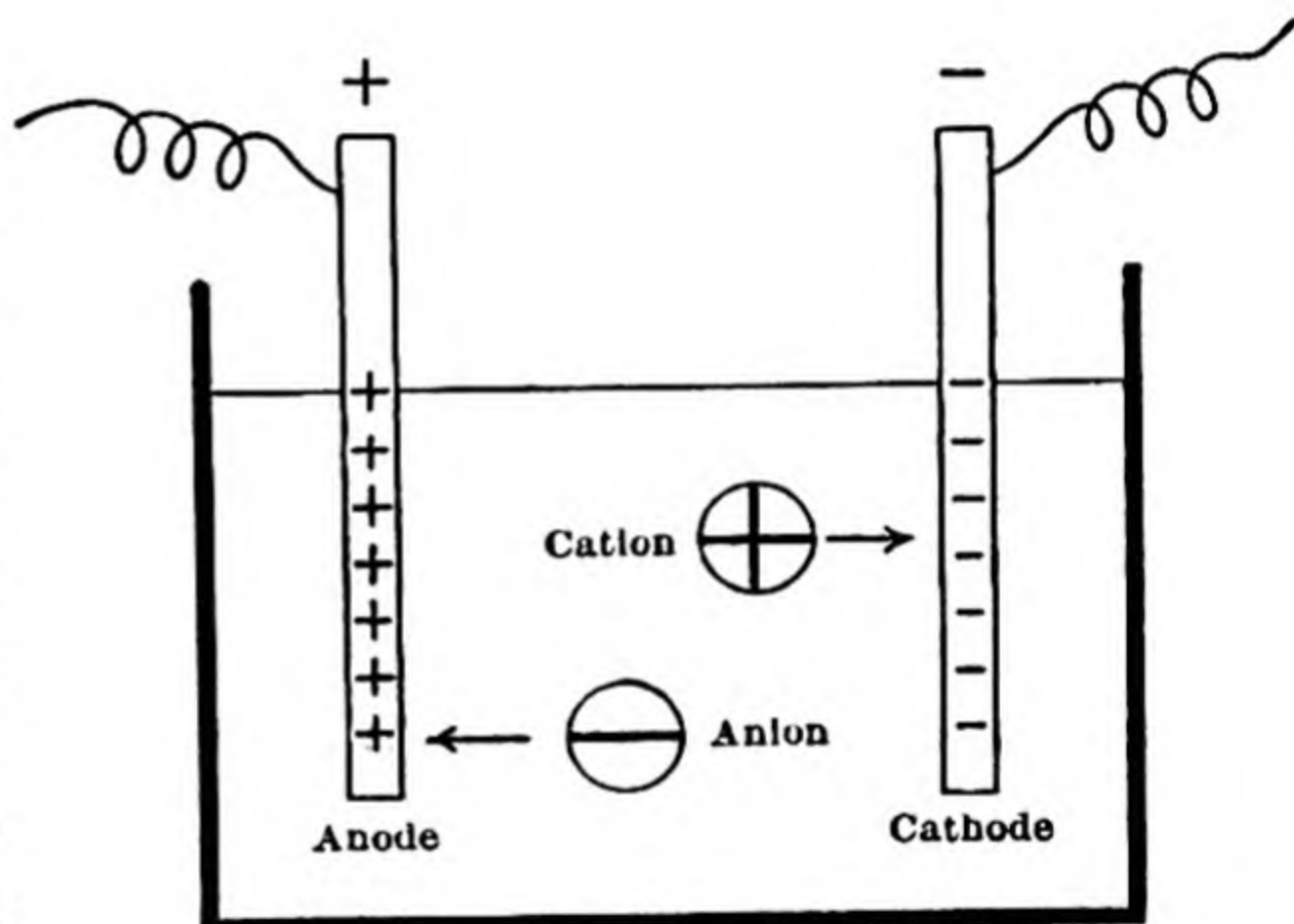
Fig. 70. Charges of Ions

charged. The particles attracted to the anode are *anions*, negative ions. Those attracted to the cathode are *cations*, positive ions. Simple nonmetal ions — such as chloride, bromide, iodide, and sulfide — and complex nonmetal ions — such as hydroxide, nitrate, and sulfate — are common anions. Ions of hydrogen and the metals are common cations.

Sodium chloride becomes dispersed into sodium ions and chloride ions when it dissolves in water. Sodium ions have positive electrovalence of 1, and chloride, negative electrovalence of 1. The solution of sodium chloride contains equal numbers of sodium and chloride ions and is electrically neutral. The sodium ion contains one electron less than the atom, and the chloride ion, one more.

The differences between these atoms and ions are indicated by the diagrams in Figs. 71 and 72, in which the electrons in each energy region are represented by a circle. Compound ions are composed of groups of atoms in which the bonding is of the covalent type, consisting of pairs of electrons. The entire group, however, contains a different number of electrons than the atoms in an uncombined condition. As in simple ions, the electric charge is positive if the number of electrons is lesser, and negative if it is greater, than in

Na·
Sodium Atom

Na⁺
Sodium Ion

Fig. 71

: Cl·
Chlorine Atom

: Cl: ⁻
Chloride Ion
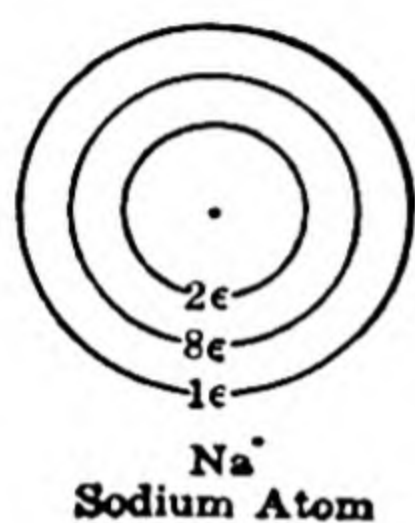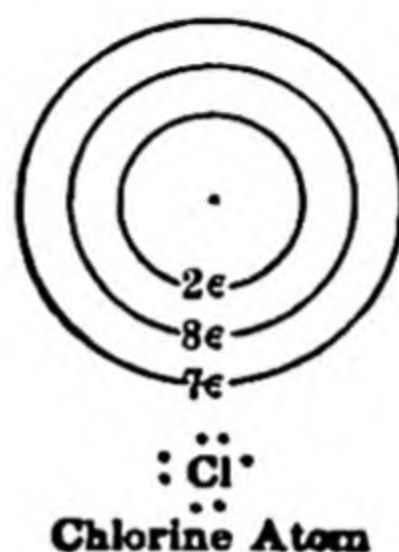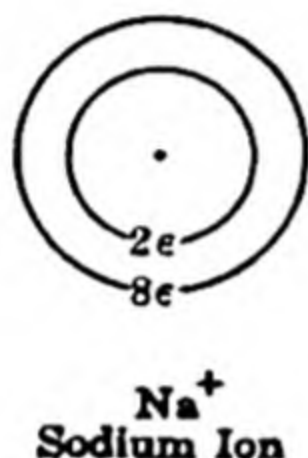
Fig. 72
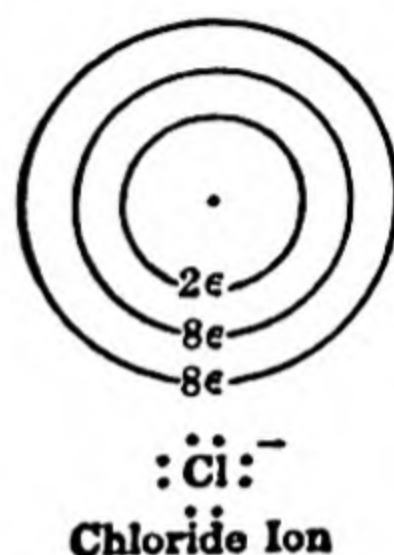
the individual atoms in the free state. The sulfate ion is composed of one sulfur and four oxygen atoms. Each of the five atoms has six valence electrons, but thirty-two are required for the ion. Hence, the sulfate ion has an electrovalence of 2 −.

The Dispersal of Salts in Water. Ionic solids dissolve in water if the forces exerted by the solvent are great enough to overcome the attraction of the ions for one another. The ions are held in position in the crystal by the forces of attraction and repulsion, which they exert upon one another because of their electrical charges. The dispersing action of water on an ionic solid may be explained in terms of the polar nature of its molecules. Water molecules are *dipoles*, particles in which the centers of positive and negative charges do not coincide. The distances separating these centers of charge in the water molecules are relatively great, and therefore the degree of polarity is relatively large. Water molecules become oriented about the ions in the surface of an ionic solid such as potassium chloride. The negative part of water molecules is attracted toward potassium ions, and the positive part, toward chloride ions. (Fig. 73.) The forces of attraction of the ions for one another are weakened, and ions separate from the face of the crystal, becoming free ions associated with molecules of water.

Even though all of the ions in solution may exist as individual particles, they exert forces due to their electric charges. The interferences caused in this manner decrease the activity of the ions, just as the attraction of molecules of gases for each other may cause deviations from Boyle's law.
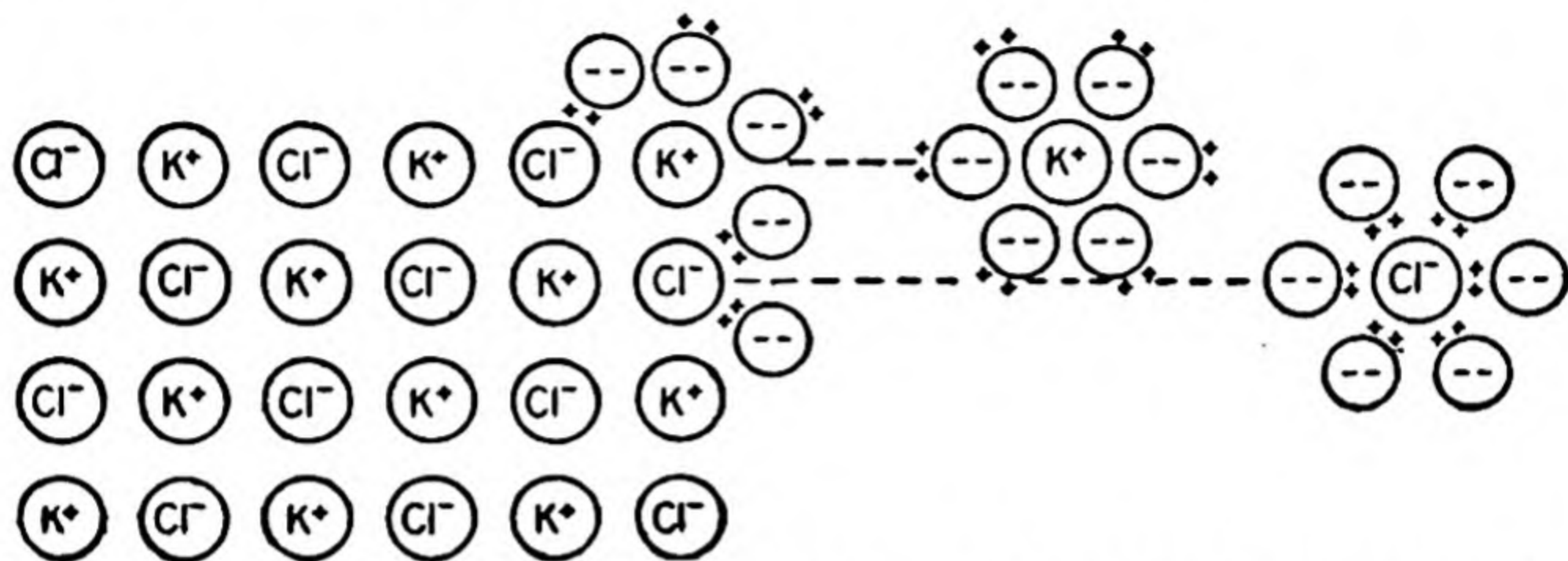
Fig. 73. *Dissolving of a Crystalline Salt in Water.* (From Hildebrand *Principles of Chemistry*, 4th Ed.)

Some of the ions moving about in solution come near the surface of the crystal and return to their appropriate positions in the crystal structure. As the concentration of the ions in solution increases, the rate of recrystallization becomes greater. When the rate of the two changes is the same, the solution is saturated. If the forces of attraction between the ions are relatively great, only low concentrations of ions in solution are required to establish equilibrium, and the solubility of the salt is slight. The hydroxides of some of the metals also yield ions by direct dispersal.

The dispersion of a solute into its ions may be expressed by an equation in which the formula represents the solid ionic material. Since these formulas do not refer to molecules, positive and negative signs may be written in the formula to indicate the charges of the ions. The charges of free ions must be indicated to differentiate them from atoms.

$$K^+Cl^- \longrightarrow K^+ + Cl^-$$
$$Na^+OH^- \longrightarrow Na^+ + OH^-$$
$$(K^+)_2SO_4^{--} \longrightarrow 2\,K^+ + SO_4^{--}$$
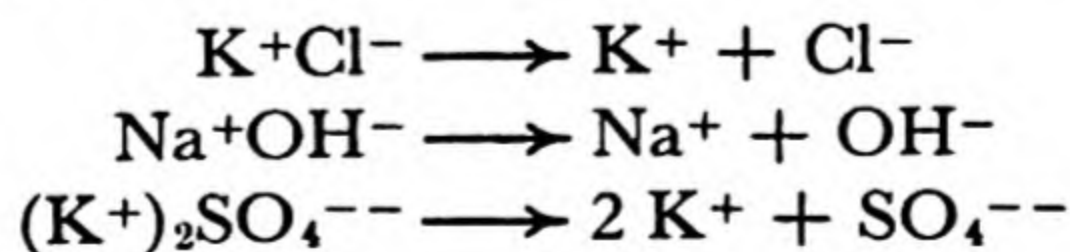
The equation representing the dispersal of potassium chloride is read: one mole of potassium chloride yields one gram ion each of potassium and chloride ions. Since ions exist as free particles in

solution, one gram ion is commonly called one mole, and a solution containing one gram ion in a liter is one molar with respect to that variety of ion.

Ionization of Molecular Substances. The common acids in pure anhydrous condition are molecular substances. Nevertheless, these substances yield ions when they dissolve in water. The formation of ions by the action of water on molecular substances is different from the dispersal of crystalline salts into ions. In 1923, both Lowry and Brönsted postulated, as part of a system of definitions concerning acids and bases in general, the formation of ions from molecular substances by interaction with the solvent.

Molecules of acids are polar in nature, with hydrogen the positive part of the molecule. Oxygen is the negative part of the water molecule. It may be assumed that the attraction between the hydrogen of the acid molecule and the oxygen of the water causes the formation of a coordinate bond when the acid dissolves in the water. In this way a complex structure may be formed, weakening the bond between hydrogen and the rest of the molecule. When this effect is sufficiently great, the hydrated acid molecule is assumed to dissociate, yielding positive hydrated hydrogen ions and negative ions — which may or may not be hydrated — composed of the remainder of the acid molecule. The simple hydrogen ion, formed by the removal of an electron from an atom of hydrogen, is a single proton. Considering that the size of the proton is small relative to its charge, it is unlikely to remain free, except temporarily as a gas ion. The hydrated proton, or ion of hydrogen, is known as the hydronium ion, H_3O^+. In terms of these assumptions, when hydrogen chloride dissolves the formation of ions may be represented by the following equation employing electronic formulas:

$$
\text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}: + \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:\text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:\text{H} + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:
$$
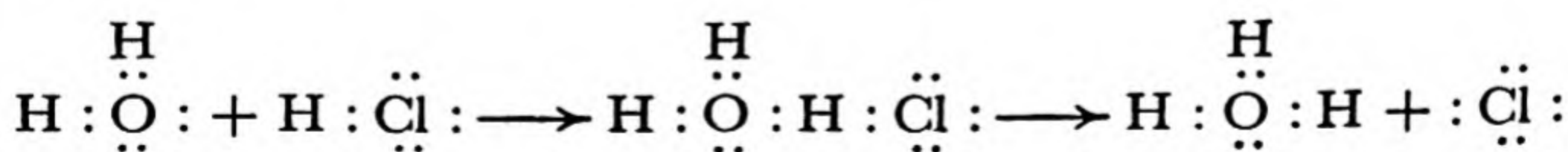
Using ordinary formulas, the equation is written:

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
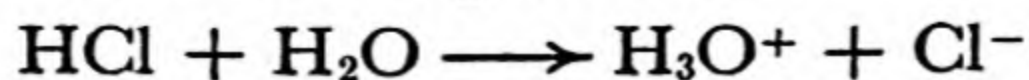
This reaction is virtually complete in very dilute solution, but is reversible in more concentrated solutions. In solutions of ordinary

concentration, a large percentage of this acid is in the ionic condition.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
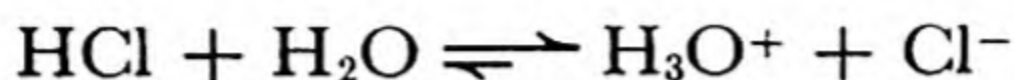
The ionization of nitric acid and of sulfuric acid may be represented by similar equations.

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$
$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$
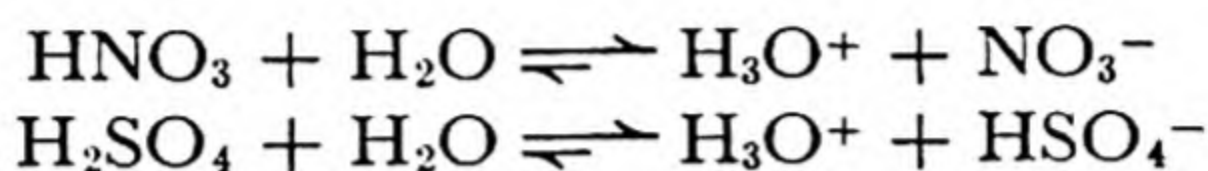
In solutions of many acids, only a small percentage of the solute is in the ionic state at equilibrium. Acetic acid is an example of an electrolyte of this type.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$
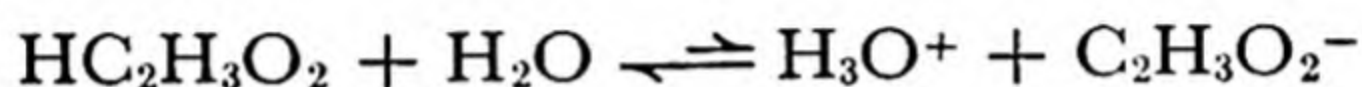
All of these reactions involve the transfer of a proton from a molecule of the acid to a molecule of water. A reaction that involves the transfer of a proton from one substance to another is called *protolysis.*

Many ions, probably most of them, are hydrated in aqueous solution. Frequently, the number of molecules of water associated with the ion is not definite. In writing equations, it is customary to omit the representation of water of hydration, unless it is essential in the process as, for example, in the formation of the hydronium ion during the ionization of acids.

The Arrhenius Theory of Ionization. In the attempt to account for the properties of electrolytes, Arrhenius in 1887 proposed a theory of ionization. The essential points in this theory may be stated in the following form:

> *Molecules of acids, bases, and salts dissociate in aqueous solution into ions which bear electric charges.*
>
> *Ionization of many solutes is practically complete in dilute solution.*
>
> *Ionization is incomplete in more concentrated solutions, and a condition of equilibrium exists between molecules of the solute and the ions which it yields.*

The theory accounts for the reactions of solutions of electrolytes in terms of ions. Each solution contains two different varieties of ions, and therefore the properties of solutions of electrolytes are additive. The vapor pressure effects, published by Raoult in 1885,

indicate incomplete ionization, because the depression caused by electrolytes is less than an integral multiple of the effects of non-electrolytes in solutions of the same molality. The idea of incomplete ionization is supported also by the fact that the conductivity of electricity is less than it should be if ionization were complete. The theory has assumed a place of fundamental importance in modern chemistry, and provoked much experimental and theoretical research. As with theories in general, its assumptions had to be modified and its limitations recognized. These modifications apply primarily to the third postulate, dealing with incomplete ionization. It has been found that the theory does not account quantitatively for the behavior of salts and other substances, largely ionic in aqueous solution. With certain modifications, the theory accounts adequately for the properties of solutions in which only a small percentage of the solute is ionic in equilibrium with the molecular solute.

The Degree of Ionization. Crystalline salts are now considered to be completely ionic in dilute aqueous solutions, even though interferences due to the charges of the ions diminish their activity. Furthermore, some molecular substances are almost completely dissociated into ions in dilute solution, but only small percentages of others are ionized. Substances completely or nearly completely ionized in dilute aqueous solution are *strong electrolytes*. Those largely in the molecular state, in equilibrium with low concentrations of ions, are *weak electrolytes*. There are other intermediate substances. The effective ion concentration corresponds to incomplete ionization in solutions of most electrolytes in concentrations usually employed in laboratory work. The term *apparent degree of ionization* indicates that percentage of the solute which would give the ionic properties observed in a completely ionized state with a remainder in molecular state. In many instances the apparent degree of ionization is the actual percentage ionized, but in solutions of many other substances, it indicates the effective ion concentration rather than the actual concentration. The apparent degree of ionization may be determined by measuring the conductivity of the solution and by comparing the value thus obtained with that which the solution would exhibit if all of the solute were ionic and there were no forces to interfere.

The apparent degree of ionization depends on the nature of both the solute and the solvent. The degree of ionization of different solutes in the same solvent may differ. Salts composed of ions having similar electrovalences exhibit approximately the same apparent degree of ionization in aqueous solutions of equal concentration, but the higher the electrovalences of the ions, the lower is the apparent degree of ionization. There are also a few substances, commonly regarded as salts, that yield only low concentrations of ions. Among these are lead acetate, the halides of cadmium and of divalent mercury, and mercuric cyanide. Similar differences are observed among the acids and the hydroxides of metals. Apparent degrees of ionization of some common solutes in aqueous solution are shown in Table 22. In the classification of salts in this table, the first number represents the electrovalence of the cation, and the second, that of the anion. Thus, potassium chloride, KCl, is an example of a 1–1 salt; potassium, K_2SO_4, a 1–2 salt; calcium chloride, $CaCl_2$ a 2–1 salt; and aluminum chloride, $AlCl_3$, a 3–1 salt.

TABLE 22. APPARENT DEGREE OF IONIZATION IN
0.1 M. SOLUTION AT 25°

Solute	Ions		Approximate Per Cent Ionized
1–1 Salts	M^+	A^-	85.0
1–2 Salts	$2 M^+$	A^{--}	73.0
2–1 Salts	M^{++}	$2 A^-$	73.0
1–3 Salts	$3 M^+$	A^{---}	65.0
3–1 Salts	M^{+++}	$3 A^-$	65.0
2–2 Salts	M^{++}	A^{--}	40.0
Sodium hydroxide	Na^+	OH^-	90.0
Potassium hydroxide	K^+	OH^-	90.0
Barium hydroxide	Ba^{++}	$2 OH^-$	80.0
Ammonia water	NH_4^+	OH^-	1.3
Hydrochloric acid	H_3O^+	Cl^-	90.0
Nitric acid	H_3O^+	NO_3^-	90.0
Sulfuric acid	H_3O^+	HSO_4^-	90.0
Oxalic acid	H_3O^+	$HC_2O_4^-$	50.0
Sulfurous acid	H_3O^+	HSO_3^-	33.0
Phosphoric acid	H_3O^+	$H_2PO_4^-$	27.0
Hydrofluoric acid	H_3O^+	F^-	8.5
Nitrous acid	H_3O^+	NO_2^-	6.5
Acetic acid	H_3O^+	$C_2H_3O_2^-$	1.33
Carbonic acid	H_3O^+	HCO_3^-	0.17
Hydrogen sulfide	H_3O^+	HS^-	0.07
Hydrocyanic acid	H_3O^+	CN^-	0.01
Boric acid	H_3O^+	$H_2BO_3^-$	0.01

The formation of ions depends on the effect of the solute and solvent on each other. Water is the most important of the ionizing solvents, but ionization occurs to a smaller degree in other solvents also, *e.g.*, methyl alcohol, ethyl alcohol, and liquid ammonia. The best ionizing solvents are composed of polar molecules. The forces exerted between two oppositely charged free particles depend not only on their charges and their distances apart but also on the nature of the medium that separates them. The *dielectric constant* is a measure of this specific property of the solvent, as related to the polar nature of its molecules. By definition, the force between two charged particles varies inversely as the dielectric constant of the separating medium. The dielectric constants of a few liquids at 18° are listed in Table 23.

TABLE 23. DIELECTRIC CONSTANTS OF A FEW SOLVENTS AT 18°

Solvent	Constant	Solvent	Constant
Water	80	Acetic Acid	9.7
Methyl Alcohol	33	Chloroform	5.0
Ethyl Alcohol	26	Diethyl Ether	4.0
Ammonia	22	Benzene	2.3

Liquids of high dielectric constant have a greater ionizing power than those of low dielectric constant.

The apparent degree of ionization of an electrolyte increases as the concentration of the solute decreases. The more dilute the solution, the greater are the average distances between ions. Consequently, the forces the ions exert upon one another are less, and a larger percentage of the solute appears to be ionic. The effect of dilution upon the apparent degree of ionization of a few solutes is shown in Table 24.

TABLE 24. EFFECT OF DILUTION ON THE DEGREE OF IONIZATION

Solution	PER CENT IONIZED AT CONCENTRATIONS OF			
	1 N.	0.1 N.	0.01 N.	0.001 N.
Hydrochloric acid	78.0	90.0	97.0	100.0
Potassium hydroxide	77.0	90.0	95.0	98.0
Potassium chloride	76.0	85.0	94.0	98.0
Copper sulfate	22.0	40.0	62.0	85.0
Acetic acid	0.4	1.3	4.1	12.1

The apparent degree of ionization of an electrolyte is affected by the presence of other ions in solution. This effect is small in dilute solutions of strong electrolytes, except in saturated solutions of substances of low solubility. If solutions of strong·and weak electrolytes containing one variety of ion in common are mixed, the concentrations of ions of the weak electrolyte are reduced to satisfy equilibrium conditions. This may be illustrated by the effect of sodium acetate on acetic acid. This acid produces a pink color with the indicator, methyl orange; an effect due to a sufficiently large concentration of hydronium ions. The pink color disappears, and the solution becomes yellow when sodium acetate is added. The concentration of acetate ions furnished by sodium acetate, a strong electrolyte, is too great to remain in equilibrium with hydronium ions and with molecular acetic acid, a weak electrolyte. Consequently, when equilibrium is reestablished a larger proportion of the acid is in the molecular state. The concentration of the hydronium ion is correspondingly reduced, becoming too low to show the pink color with methyl orange. *The degree of ionization of a weak electrolyte is decreased by the addition of a strong electrolyte which yields ions common to both substances.*

Weak Electrolytes. Ionization Constants. The degree of ionization of weak electrolytes in aqueous solution is low, and such solutions are poor conductors of electric current. Equilibrium exists in the solution when the velocity of the ionization reaction is equal to the velocity of the reaction producing the molecular substance. The ionization of acetic acid is represented by the equation:

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$
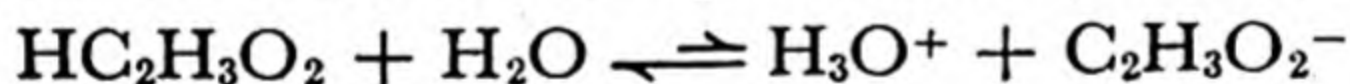
The relationships of the concentrations at equilibrium may be shown by an equilibrium constant. (See page 130.)

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2] \times [H_2O]} = K$$

The molar concentration of water, *i.e.*, the number of moles in one liter, is so nearly the same in dilute solutions and in pure water that no significant error is introduced by assuming that it is actually constant and omitting it in the equilibrium ratio.

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_{ionization}$$

The ionization constant of a weak electrolyte is equal to the ratio of the product of the molar concentrations of its ions to the molar concentration of the molecular substance in solution, provided that each concentration is raised to the power shown by the coefficient of that substance in the equilibrium equation. The numerical value of the constant is characteristic of the nature of the substance, and is independent of changes in concentration. It is altered by changes in temperature and also by the presence of other ions in solution, especially if their concentrations are great.

The degree of ionization of acetic acid in one molar at 18° is 0.42 per cent. The concentration of each variety of ion is 0.0042 molar and of molecular acetic acid, 0.9958 molar. Substituting these concentrations in the above formula, the ionization constant of acetic acid is found to be:

$$\frac{0.0042 \times 0.0042}{0.9958} = K = 0.0000177 = 1.77 \times 10^{-5}$$

The degree of ionization of this substance in 0.1 molar solution is 1.33 per cent. The concentration of each ion in this solution is 0.00133 molar and of the molecular acid, 0.09867 molar.

$$\frac{0.00133 \times 0.00133}{0.09867} = 1.78 \times 10^{-5}$$

The ionization constants of a number of weak electrolytes are shown in the Appendix, Table X.

The concentration of a particular variety of ion in a solution of given molarity may be calculated from the ionization constant of the substance. Suppose that the concentration of hydronium ions in a 0.2 M. solution of hydrocyanic acid is to be calculated.

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$
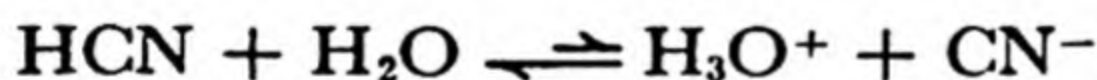
From the tabulated data, the ionization constant of this acid at 25° is 4×10^{-10}.

$$\frac{[H_3O^+] \times [CN^-]}{[HCN]} = K = 4 \times 10^{-10}$$

Let C represent the concentration of hydronium ions in this solution. Then C also represents the concentration of cyanide ions and $0.2 - C$, the concentration of molecular hydrocyanic acid.

$$\frac{C \times C}{0.2 - C} = 4 \times 10^{-10}$$

$$C^2 = 4 \times 10^{-10} \times (0.2 - C)$$

The ionization constant of this acid is so small that the difference between $(0.2 - C)$ and 0.2 is negligible. Therefore,

$$C^2 = 4 \times 10^{-10} \times 0.2 = 0.8 \times 10^{-10}$$
$$C = \sqrt{0.8 \times 10^{-10}} = 9 \times 10^{-6}$$

If the concentration of the undissociated solute differs significantly from the entire concentration of the solute, this difference may not be ignored and the calculation cannot be simplified in this manner.

Common Ion Effect. The degree of ionization of a weak electrolyte is decreased by the addition of another solute that furnishes an ion in common. Suppose that sodium acetate is added to an acetic acid solution in sufficient quantity to maintain the concentration of the acetate ion at one molar. It is apparent that the concentration of the hydronium ion cannot remain equal to 0.0042 M., because

$$\frac{0.0042 \times 1}{0.9958} > 1.8 \times 10^{-5}$$

Consequently, the concentrations become adjusted to a new state of equilibrium, with a smaller concentration of hydronium ions and a larger concentration of the undissociated acid. The additional concentration of acetic acid is small compared to 0.9958. Hence, the concentration of the hydronium ion is decreased to approximately the same degree as the acetate ion concentration is increased. Under the conditions stated above, the concentration of the hydronium ion would be decreased to approximately 1.7×10^{-5} molar.

The common ion effect is an important means of regulating ion concentrations in solutions of weak electrolytes at some specific low value. The high concentration of the molecular weak electrolyte serves as a source of its ions, thus preventing a significant decrease in this regulated concentration. The large concentration of one of the ions of the weak electrolyte prevents any significant increase in the concentration of the other ion it furnishes. This effect is important in establishing the most favorable conditions for many reactions.

Strong Electrolytes. Interionic Attraction. Strong electrolytes are completely or nearly completely ionized in dilute aqueous solutions. Nevertheless, the apparent degree of ionization, measured by conductivities and by freezing point effects, is less than corresponds to complete ionization. The behavior of strong electrolytes, in respect to their ionic properties, is now explained in terms of the *interionic attraction theory*. The quantitative aspects of this theory are beyond the scope of this text. The forces of attraction of the oppositely charged particles of an ionic solid are weakened by the action of the solvent, but are not eliminated. The forces of attraction of such particles in a solution vary directly with the product of the charges and inversely with the square of the distances between them. As the average distance between particles increases with the dilution of the solution, the forces of attraction diminish. When the effects have become nonexistent, the solution is called *infinitely dilute*.

The attractions between the ions interfere with their freedom of motion, and cause a decrease in the effective or apparent degree of ionization. This leads to a diminished effect on the vapor pressure of water, a lower conductivity of electricity, and a decreased chemical activity. The introduction of activity coefficients expressing intermolecular forces has been discussed in connection with deviations from Raoult's law, in Chapter 7, page 115. On the basis of the interionic effects, Debye and Hückel calculated the activity coefficients for dilute solutions of many strong electrolytes. The product of the molality and the activity coefficient gives a corrected concentration value known as the *activity*.

EXERCISES

1. Cite evidence to show that the numbers of particles per mole are greater in aqueous solutions of salts, acids, and basic hydroxides than in solutions of sugars.
2. What is the nature of the particles in aqueous solutions of electrolytes? How may this be shown experimentally?
3. Define electrolyte, nonelectrolyte, anion, and cation.
4. Write electronic formulas to represent the following: (*a*) sodium atoms and sodium ions; (*b*) calcium atoms and calcium ions; (*c*) aluminum atoms and aluminum ions; (*d*) chlorine and chloride ions; (*e*) sulfur and sulfide ions; (*f*) sulfur and sulfate ions; (*g*) iodine and iodate ions; (*h*) hydrochloric acid and sodium chloride; (*i*) sodium ions and neon atoms.

5. What are the structural units of crystalline salts?
6. Describe the changes assumed to occur during the dissolving of a salt such as sodium sulfate.
7. Account for the ionization of hydrochloric acid and sulfuric acid.
8. What is meant by a dipole? hydronium ions? a weak electrolyte? a strong electrolyte?
9. State the assumptions of the Arrhenius theory of ionization, and give experimental evidence to support each assumption.
10. What is meant by the apparent degree of ionization? What conditions affect the apparent degree of ionization, and what is the effect of each?
11. What is meant by an ionization constant? the common ion effect?
12. How is the apparent incomplete ionization of strong electrolytes explained?

SUPPLEMENTARY READINGS

Hildebrand, J. H., *Principles of Chemistry*, 4th Ed., The Macmillan Company, New York, 1940, chaps. VIII, XII, XIII.

Hammett, L. P., *Solutions of Electrolytes*, McGraw-Hill Book Company, Inc., New York, 1936, pp. 3–17; 46–68.

Creighton, H. J., and W. A. Koehler, *Electrochemistry*, John Wiley & Sons, Inc., New York, 1935, Vol. I, chaps. III–IV.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, American Book Company, New York, 1936, chap. VIII.

Arrhenius, S. A., "Electrolytic Dissociation," *J. Am. Chem. Soc.* 34, 353 (1912).

Davidson, A. W., "Solutions of Electrolytes," *J. Chem. Education* 12, 24 (1935).

Scatchard, G., "The Coming of Age of the Interionic Attraction Theory," *Chemical Reviews* 13, 7 (1933).

Chapter 15

DISPLACEMENT OF IONS. ELECTROLYSIS. ELECTRIC CELLS

Ions are the active particles in a great number of chemical reactions. Many ionic reactions involve oxidation-reduction, the transfer of electrons with corresponding changes in oxidation numbers. In this chapter, the relationships between elementary substances and the ions they produce are emphasized in the consideration of three types of ionic phenomena which involve oxidation-reduction.

Displacement of Metal Ions. In a preceding section, page 59, the displacement of hydrogen from acids and of metals from salt solutions has been discussed. The displacing metal must have a greater activity in loss of electrons than the metal displaced. The ionic equation representing the reaction of zinc with sulfuric acid may be written:

$$Zn + 2\,H^+ + SO_4^{--} \longrightarrow Zn^{++} + H_2 + SO_4^{--}$$
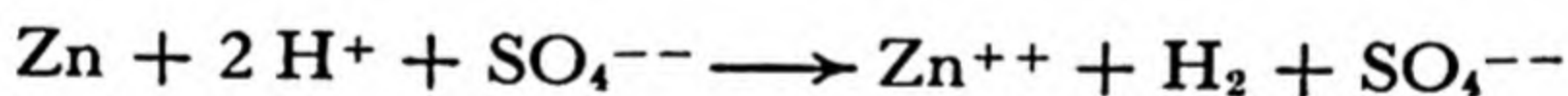
It is evident that sulfate ions are not affected during this reaction. Consequently, they are omitted from the ionic equation.

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$$
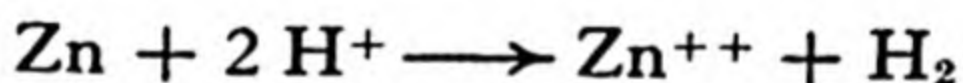
During this reaction, zinc atoms give up electrons to form ions, and hydrogen ions gain electrons to form hydrogen. The electronic nature of these changes may be shown by writing two partial equations: one for the gain of electrons, a reduction process, and the other for the loss of electrons, an oxidation process. These partial equations are called ion-electron equations. Each represents a half reaction and, consequently, neither occurs without the other. The complete equation for the reaction is obtained by adding the two partial equations, with cancellation of the electrons represented on both sides. This procedure may be illustrated by the partial

equations showing the electron changes in the reaction of zinc with sulfuric acid. In these equations, the electron is represented by the Greek letter epsilon ϵ.

$$\begin{array}{r} 2\,H^+ + 2\,\epsilon \longrightarrow H_2 \\ Zn \longrightarrow Zn^{++} + 2\,\epsilon \\ \hline 2\,H^+ + Zn \longrightarrow H_2 + Zn^{++} \end{array}$$
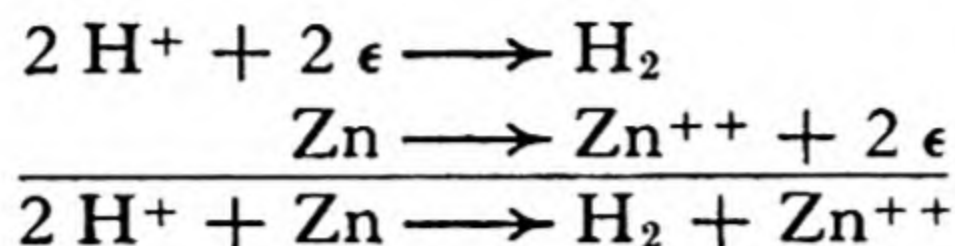
Each partial equation must be completely balanced within itself, and no surplus of electrons may remain in the final equation obtained by the addition of the partial equations. Consequently, if the numbers of electrons shown in the unit processes are not equal, each partial equation is multiplied by an integer so as to make the total numbers equal. Then the partial equations may be added. This is illustrated by the equation for the reaction of aluminum with a solution of cupric sulfate.

$$\begin{array}{r} [Cu^{++} + 2\,\epsilon \longrightarrow Cu] \times 3 \\ [Al \longrightarrow Al^{+++} + 3\,\epsilon] \times 2 \\ \hline 3\,Cu^{++} + 2\,Al \longrightarrow 3\,Cu + 2\,Al^{+++} \end{array}$$
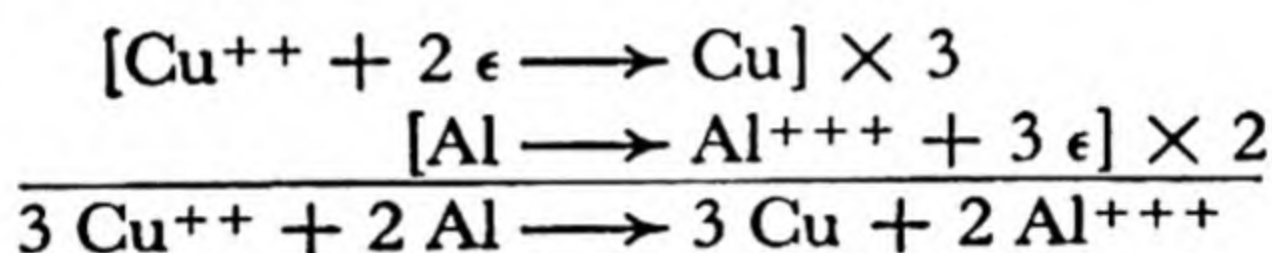
This method of deriving the equation is known as the *ion-electron method*. The steps involved should be clearly understood by repeated application to simple oxidation-reduction processes, for the method is found to be very useful in dealing with more complex processes.

In these equations, it is observed that the metals serve as sources of electrons. Substances that release electrons during chemical reactions are *reducing agents*. Metal ions may gain electrons, becoming reduced to the free metal. Substances which gain electrons in chemical reactions are *oxidizing agents*. Oxidation and reduction are processes of an opposite nature. A metal, which is an active reducing agent, yields ions that are relatively stable toward reduction. Hence, the ions of active metals are not good oxidizing agents.

Displacement of Simple Nonmetal Ions. The displacement of bromine from bromides by the action of chlorine has been discussed as a source of bromine on page 159. Chlorine is a more active nonmetal than bromine, because its atoms gain electrons more readily. The equation for this displacement reaction may be derived by the ion-electron method in the following manner:

$$Cl_2 + 2\,\epsilon \longrightarrow 2\,Cl^-$$
$$\underline{\qquad 2\,Br^- \longrightarrow Br_2 + 2\,\epsilon \qquad}$$
$$Cl_2 + 2\,Br^- \longrightarrow 2\,Cl^- + Br_2$$
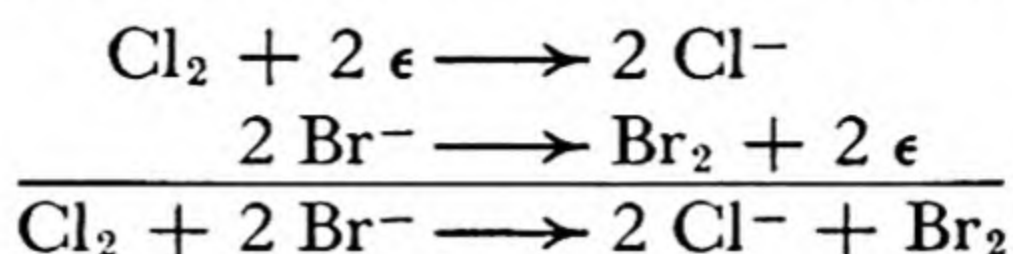
Nonmetals of high activity are good oxidizing agents because their atoms readily gain electrons. Conversely, simple nonmetal ions formed by active nonmetals are more stable toward oxidation than similar ions of less active nonmetals. The properties of metals and nonmetals are directly opposite in this respect. In terms of the theories of atomic structure, the atoms of active metals contain one or two valence electrons, while the atoms of active nonmetals require only one or two electrons to complete the valence shell.

ELECTROLYSIS

The passage of a direct current of electricity through a solution of an electrolyte is accompanied by the migration of ions toward the electrodes bearing the opposite charges. Electrodes are usually strips or bars of solid electrical conductors, such as inactive metals or graphite, connected by conducting wires to the source of current. Positive ions gain electrons at the cathode and thus become reduced to elementary particles. Simultaneously, negative ions lose electrons at the anode and are oxidized. The transfer of electrons through an electrolytic conductor is accomplished in this manner. The entire process, the migration of ions and the reactions at the electrodes, is known as *electrolysis*.

An electric current flows through a circuit when the electromotive force is great enough to overcome the resistance of the conductor. When a current flows through a solution, ions must move against the attracting forces exerted by the ions of opposite charges. The oxidation-reduction reactions which take place at the electrodes are reversible. Hence, the electromotive force, or difference in electrical potential, must be great enough to overcome these opposing forces and cause the process to continue. The unit of electromotive force, *the volt*, is that difference in potential between two points, which causes a current to flow at the rate of one ampere when the resistance of the conductor is one ohm. *The ohm*, the unit of resistance, is by definition the resistance at 0° of a column of mercury 106.300 cm. long and of such cross section that it weighs

14.4521 g. *The ampere* is the unit of current strength, one coulomb per second, and one *coulomb* is the amount of electricity required to deposit 0.0011180 g. of silver from a solution of a silver salt.

Products of Electrolysis. The nature of the products obtained at the electrodes depends on the nature of the ions in solution. Aqueous solutions contain not only the ions of the solute, but also low concentrations of hydronium and hydroxide ions from water. Cations of metals that do not actively displace hydrogen from water are reduced at the cathode during the electrolysis of various salt solutions. Hydrogen is displaced instead of metal from salt solutions containing ions of active metals, because hydronium ions are reduced at lower electrical potentials than ions of these metals. Simple anions are oxidized at the anode unless hydroxide ions of water may be oxidized at lower potentials. Compound ions, such as sulfate and nitrate, are not discharged directly during the electrolysis of salt solutions, but hydroxide ions are oxidized to form oxygen and water. The products formed by the direct discharge of ions from a solution are known as the *primary products of electrolysis*. The description of the electrolysis of specific salt solutions illustrates the principles involved.
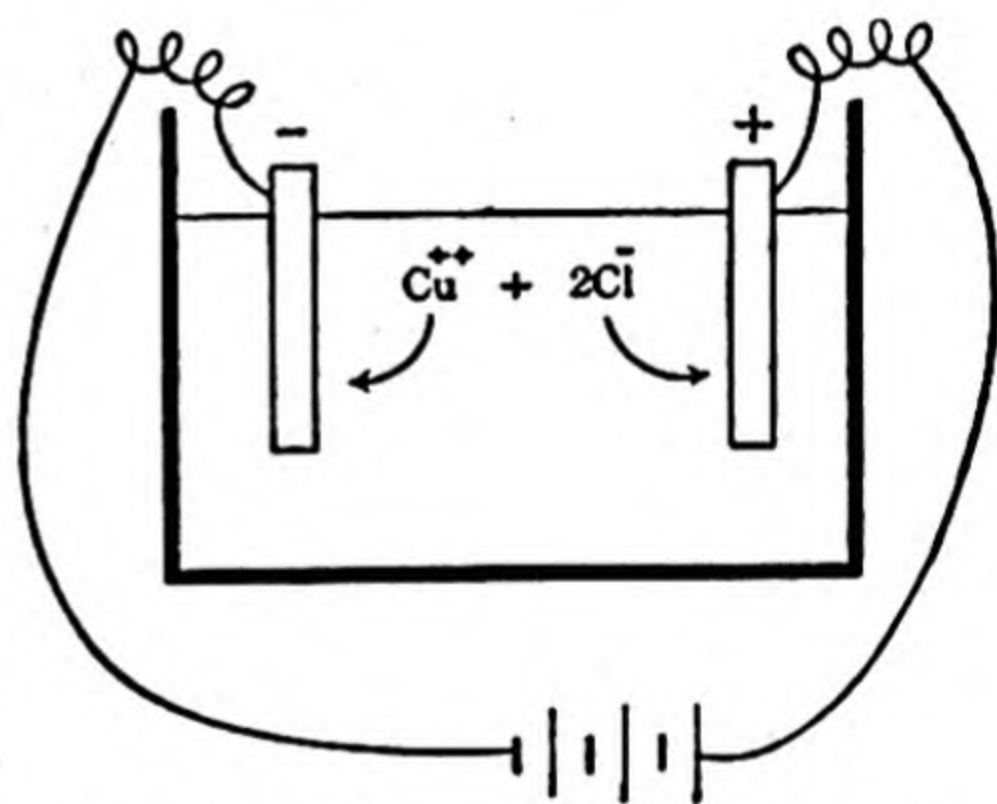
Fig. 74. Diagram. Electrolysis of Cupric Chloride Solution

The discharge of ions of the solute at both anode and cathode is illustrated by the electrolysis of a solution of cupric chloride, using inactive electrodes. The salt is dispersed into ions when it dissolves. During the passage of the current, cupric ions migrate to the cathode and chloride ions to the anode. (Fig. 74.) Each cupric ion reduced gains two electrons, and metallic copper is deposited on the cathode. The cathode reaction is shown by the ion-electron equation:

$$Cu^{++} + 2\,\epsilon \longrightarrow Cu$$
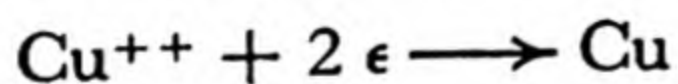
An equivalent number of chloride ions become oxidized at the anode, and elementary chlorine is produced.

$$2\,Cl^{-} \longrightarrow Cl_2 + 2\,\epsilon$$
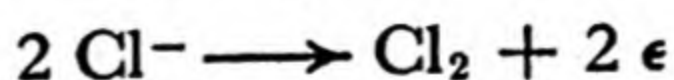
These two processes occur in different parts of the cell, and a single equation obtained by adding the two partial equations has little meaning. However, they are not entirely independent, as the total number of electrons involved is the same at each electrode. Although the solution contains low concentrations of hydronium and hydroxide ions, these ions are not discharged to a significant degree during the process, since the cupric and chloride ions are discharged at the lower electrical potentials.
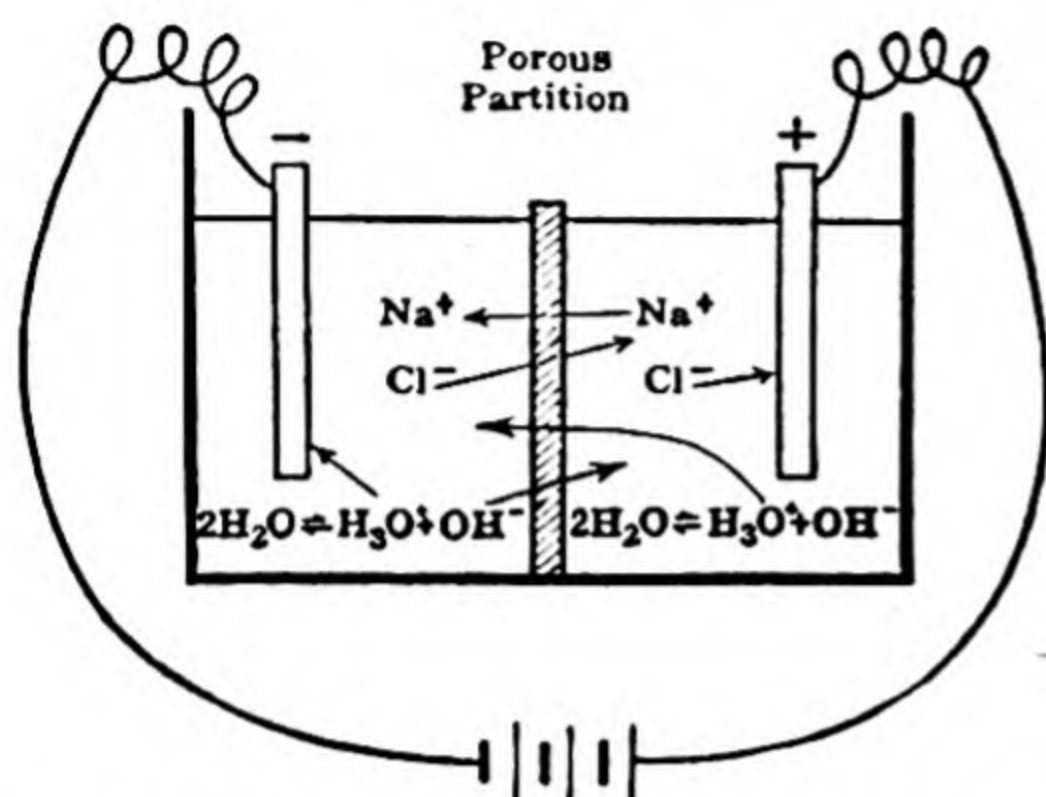
Fig. 75. Diagram. Electrolysis of Sodium Chloride Solution

The discharge of hydronium ions occurs at the cathode during electrolysis of sodium chloride solutions. Both sodium and hydronium ions migrate to the cathode, and chloride and hydroxide ions to the anode. (Fig. 75.) Hydronium ions are less stable toward reduction than sodium ions, and elementary hydrogen is evolved at the cathode.

$$2\,H_3O^+ + 2\,\epsilon \longrightarrow H_2 + 2\,H_2O$$

Chloride ions are oxidized at the anode as in the electrolysis of cupric chloride solutions.

$$2\,Cl^- \longrightarrow Cl_2 + 2\,\epsilon$$
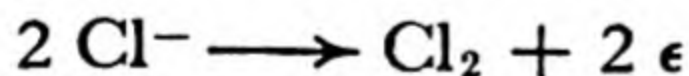
Hydroxide ions accumulate in the solution about the cathode as the hydronium ions are discharged. Free chlorine reacts with hydroxide ions if the solutions become mixed. Hence, a special type of cell, separated into anode and cathode compartments by a porous partition, is used in the

Fig. 76. Diagram. Electrolysis of Potassium Sulfate Solution

industrial preparation of sodium hydroxide and chlorine. (See page 152.)

The discharge of the ions of water at both the anode and the cathode occurs during the electrolysis of solutions of potassium sulfate. The migra-

tion of ions takes place as previously described. (Fig. 76.) Hydrogen is produced at the cathode as in the electrolysis of sodium chloride solutions.

$$2 H_3O^+ + 2 \epsilon \longrightarrow H_2 + 2 H_2O$$
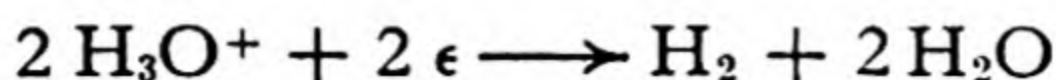
Hydroxide ions are oxidized at a lower electrical potential than required for sulfate ions, forming oxygen and water.

$$4 OH^- \longrightarrow O_2 + 2 H_2O + 4 \epsilon$$
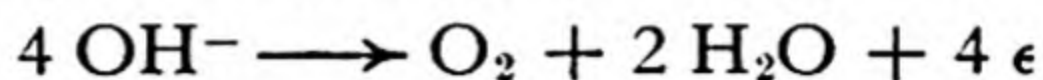
The electrolysis of solutions of this type leads to the decomposition of water, producing hydrogen and oxygen in the volume ratio of two to one.

Electrolysis may be carried out using an anode composed of the same metal as the cations of the salt. If a solution of cupric sulfate is electrolyzed using a copper anode (Fig. 77) migration of ions and deposition of copper occurs as already described.

$$Cu^{++} + 2 \epsilon \longrightarrow Cu$$
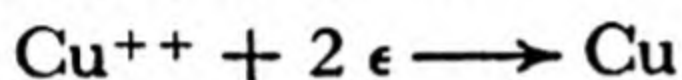
At the anode, however, the formation of cupric ions occurs at lower potential than the discharge of hydroxide ions.

Fig. 77. Diagram. Electrolysis of Copper Sulfate Solution with Copper Anode

$$Cu \longrightarrow Cu^{++} + 2 \epsilon$$

This process causes the transportation of copper from the anode to the cathode without significant change in the concentrations of the ions in the electrolyte. This arrangement of the materials for electrolysis is the basis of electroplating and the electro-refining of the metals.

In a number of instances, the primary products of electrolysis are not obtained. *Secondary products* may be formed by the reaction of the primary products with materials present in solution or by oxidation and reduction processes which do not produce molecular materials. Examples of such changes will be encountered in other sections of this text.

Faraday's Law. The relation between the quantity of electricity passing through a solution and the weights of the products formed

at the electrodes was determined by Faraday in 1833. This relation may be stated as **Faraday's Law: The quantities of substances set free at the electrodes are directly proportional to the amount of electricity passing through the solution. The same amount of electricity liberates weights of different substances, which are proportional to their equivalent weights.** The measurement of these quantities may be used for the determination of the equivalent weights of the substances produced by electrolysis, and of the charges of the ions in solution. If an electric current is passed through separate solutions of cupric sulfate, silver nitrate, and hydrochloric acid connected in series (Fig. 78), it is found that
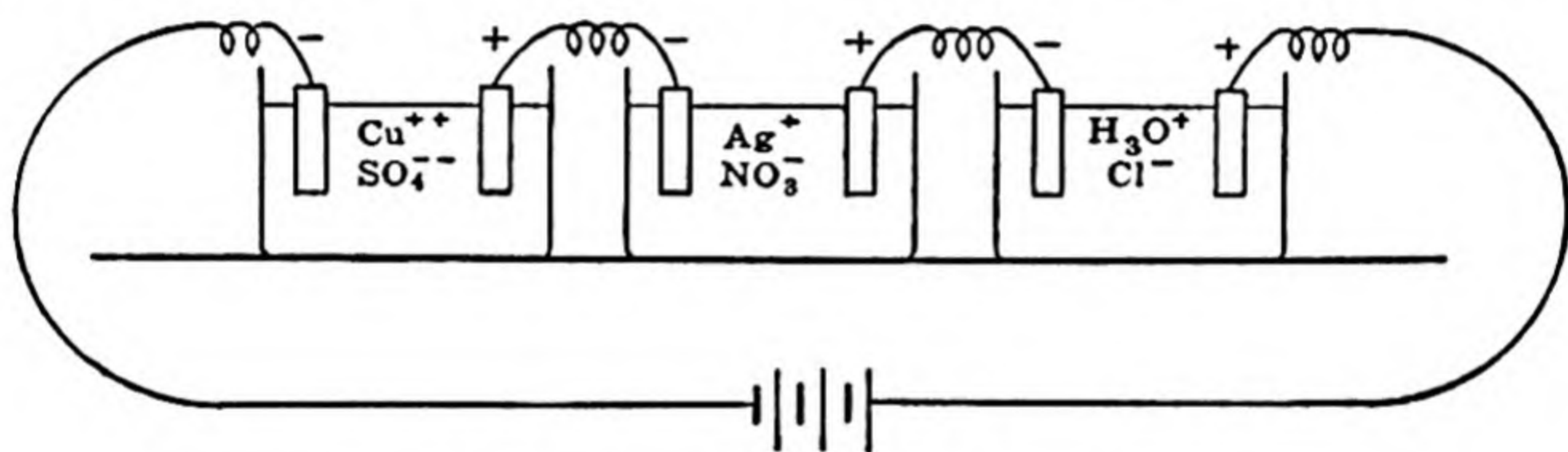
Fig. 78. Diagram Illustrating Faraday's Law

96,500 coulombs of electricity set free 31.78 g. of copper, 107.88 g. of silver, and 1.008 g. of hydrogen at the respective cathodes. Each hydronium ion requires one electron to discharge it from the solution. In the gram equivalent of hydrogen there are 6.064×10^{23} atoms, and a gram ion contains this number of hydronium ions. Therefore, 96,500 coulombs is a sufficient quantity of electricity to supply one electron for each ion in a gram ion of a substance. Since 96,500 coulombs of electricity deposit one gram atom of silver, it follows that the gram equivalent of this metal contains 6.064×10^{23} atoms. Since only one half of an atomic weight of copper is deposited by the same amount of electricity, it is necessary to conclude that each cupric ion requires two electrons to convert it into a neutral atom, and that the charge of this ion is 2. Chlorine is produced at the anode in one of these cells and oxygen in the other two. It is found that 96,500 coulombs of electricity liberate one gram atom of chlorine, but only half of one gram atom of oxygen. The quantity of electricity, 96,500 coulombs, required to set free one gram equivalent of a substance is known as one faraday.

The weights of substances deposited by a current of known amperage in a specified time may be calculated by the application of Faraday's law. If a current flowing at the rate of $1\frac{1}{2}$ amperes is passed through a solution of cupric sulfate for two hours and it is assumed that the only reaction at the cathode is the discharge of cupric ions, the weight of copper deposited may be calculated in the following manner:

The quantity of electricity $= 2 \times 60 \times 60 \times 1.5$
$= 10,800$ coulombs

The gram equivalent of copper $= 63.57/2 = 31.78$ g.
96,500 coulombs deposit 31.78 g. of copper,

10,800 coulombs deposit $\dfrac{31.78 \times 10,800}{96,500}$

$= 3.556$ g. of copper

ELECTRIC CELLS

Oxidation-reduction reactions involving ionic materials are accompanied by a transfer of electrons. In some of these reactions, such as those occurring during electrolysis, electrical energy is converted into chemical energy, and the products contain greater amounts of chemical energy than the initial substances. Many displacement reactions occur spontaneously with the evolution of energy when the substances are brought together in solution. The electrons pass directly from the reducing agent to the oxidizing agent, and the energy of the reaction is manifested as heat.

Electrical Energy from Chemical Reactions. The chemical energy of oxidation-reduction reactions involving ionic materials may be transformed into electrical energy. An electric current may be secured from such reactions by arranging the materials in a cell, so that electrons pass through an external circuit instead of directly from reducing to oxidizing agent. The arrangement of the materials for this purpose is shown diagrammatically in Fig. 79. The cell is divided into two compartments by a porous partition that permits the migration of ions, but prevents mechanical mixing. The oxidizing and reducing agents are placed in separate compartments of the cell. The materials are then connected electrically through suitable electrodes, conducting wires, and

solutions of ionized substances. If one of the materials is a solid metal, such as zinc, it may serve as one of the electrodes, but an

Fig. 79. Diagram of an Electric Cell

ionic solution must be put into the compartment along with the zinc. The oxidizing action at the one electrode releases electrons, and the reducing action at the other takes up electrons. Electrons now flow over the conducting wire if the activities of the substances are great enough. The migration of ions through the porous partition maintains equivalent concentrations of positive and negative ions in the two parts of the cell, thus completing the internal circuit.

Many cells have been developed for securing an electric current from chemical reactions. These are called *galvanic cells*. A number of different displacement reactions and other more complex oxidation-reduction processes may be used practically in cells. Displacement reactions are the simplest of these, and the present discussion will deal primarily with cells based on this type of reaction. However, the same principles are applied in the arrangement of materials for more complex reactions.

Electrode Potential. The difference in potential between two electrodes in a cell depends on the electrical condition of each. The nature of the changes that occur at the surface of an electrode determine its electrical condition. *Active metals* form ions by the loss of electrons. When a metal, such as zinc, is placed in a dilute solution of one of its salts, the formation of positive ions occurs with an accumulation of electrons on the surface of the metal. It may be assumed that the negative
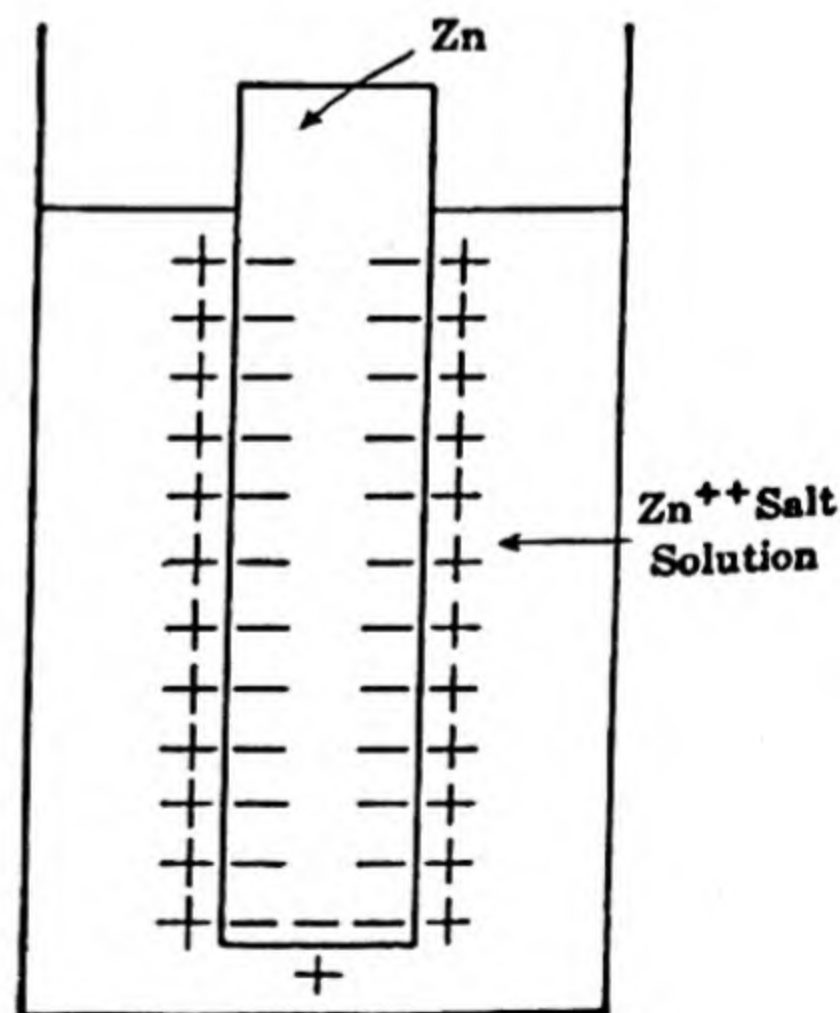
Fig. 80

charge developed in this manner prevents the uniform dispersal of ions throughout the solution. The resulting condition may be represented graphically as an electrical double layer, with an excess of electrons on the surface of the metal and an excess of ions in the adjacent solution. (Fig. 80.) Equilibrium is established when ions are being formed and discharged at the same rate.

$$Zn \rightleftharpoons Zn^{++} + 2\,\epsilon$$
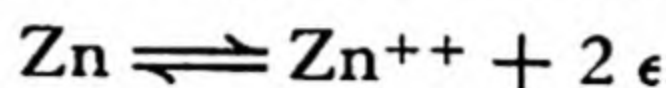
When the concentration of zinc ions is high a smaller number of free electrons is required for equilibrium than when it is low. The charge developed at an electrode composed of an active metal depends on the activity of the metal. It is increased by a rise in the temperature and decreased by an increase in the concentration of the metal ions in the solution.

To establish equilibrium, *metals of low activity* require only a low concentration of ions in solution in immediate contact with the metal. When a metal such as copper is placed in a solution of one of its salts, the concentration of ions is greater than equilibrium permits, and the deposition of some of its ions occurs, gaining electrons. This leaves a deficiency of electrons at the surface of the metal so that the electrode has a positive charge and
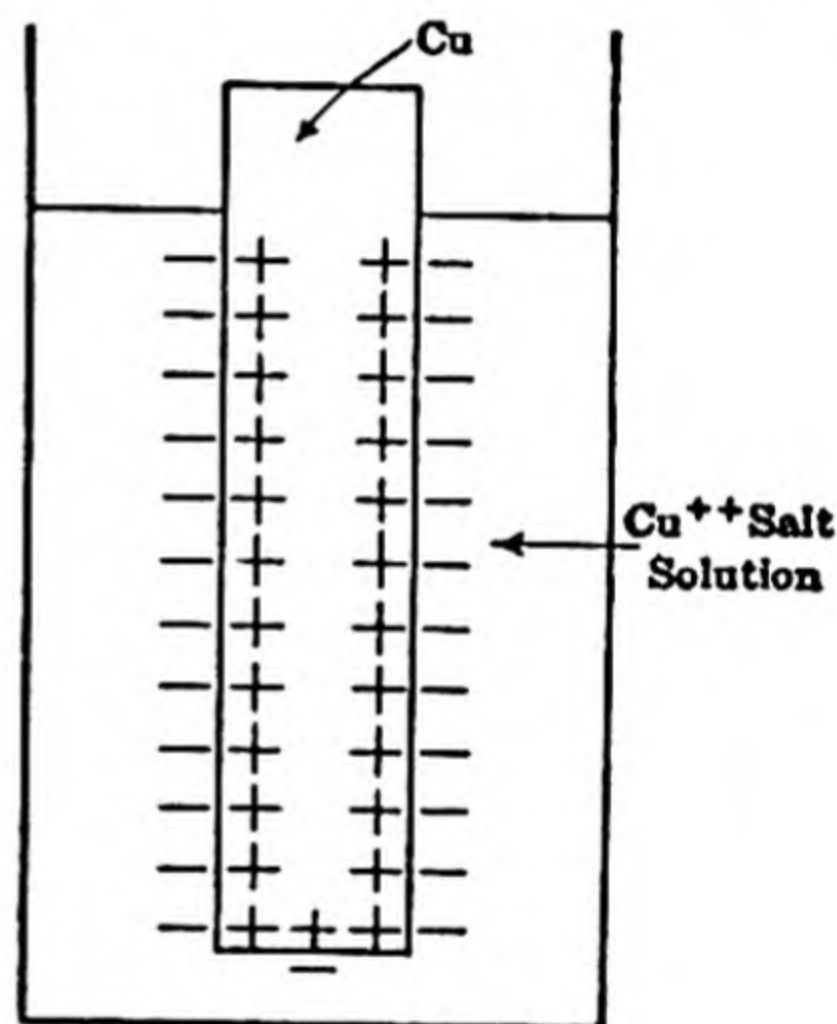
Fig. 81

repels other positive ions in the solution. Consequently, there is an excess of negative ions in the solution in the immediate vicinity of the metal. This condition may also be represented by an electrical double layer. (Fig. 81.) A state of equilibrium exists when the charge of the metal has become adjusted to the low concentration of its ions in the adjacent solution.

$$Cu^{++} + 2\,\epsilon \rightleftharpoons Cu$$
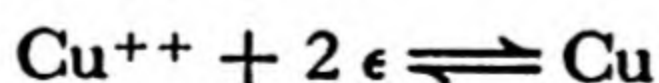
The charge on this electrode depends on the activity of the positive ions toward reduction and on the temperature. For metals of low activity, the electrode potential increases as the concentration of its ions in solution increases.

The difference in potential between pairs of electrodes in a cell may be measured experimentally, but there is no method for the direct measurement of the potential of any single electrode, because its electrical condition is disturbed as soon as connections are made in an attempt to do so. In order to bring the electrode potentials developed by different oxidizing and reducing agents into a related system, *a reference electrode* is adopted, and the potential differences between other electrodes and the reference electrode are measured. An electrode made of platinum, coated with platinum black or finely divided platinum, and saturated with hydrogen gas at a pressure of one atmosphere in a solution of hydronium
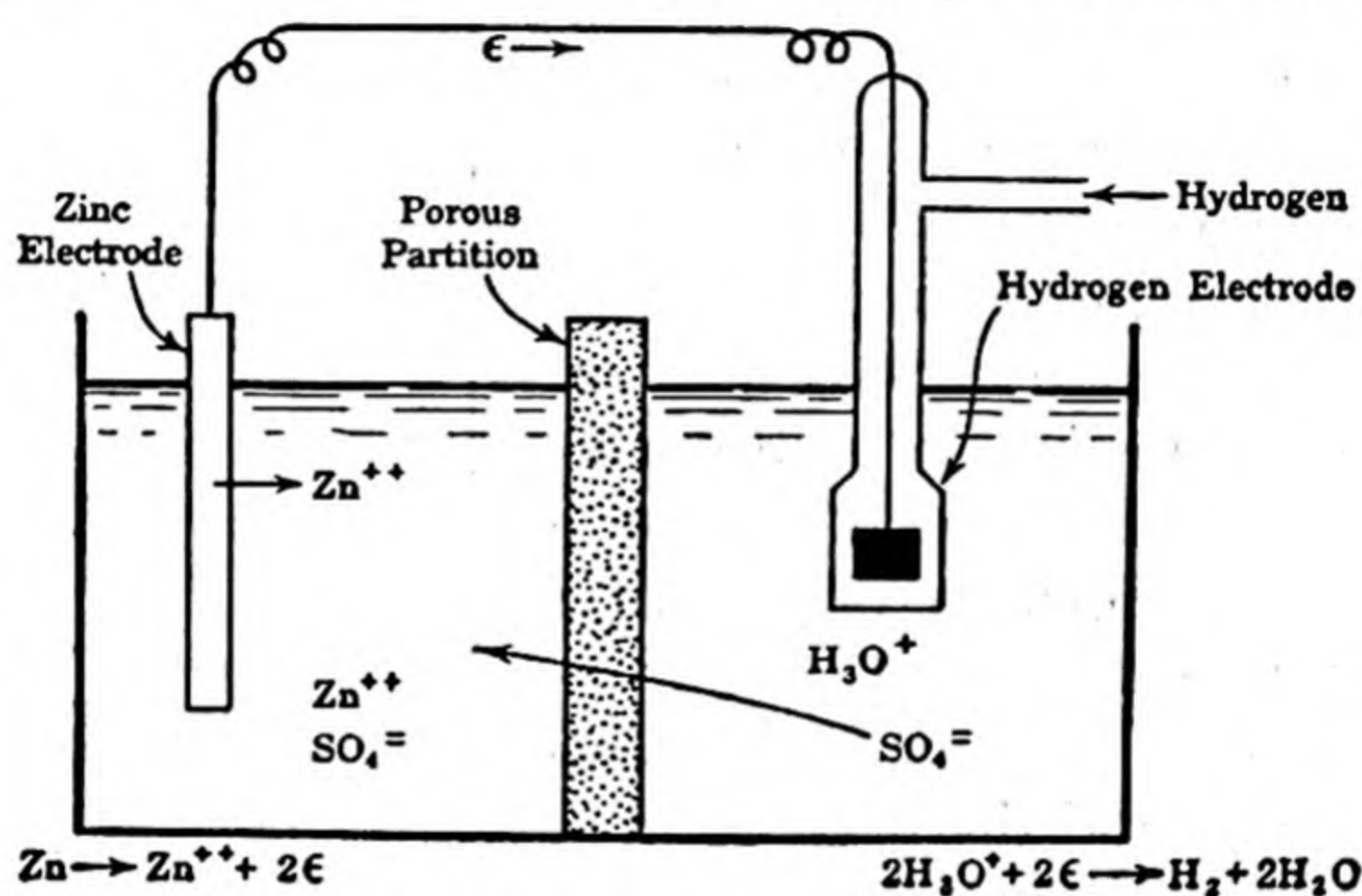
Fig. 82. Hydrogen Electrode

ions of unit activity is known as *the hydrogen electrode*. (Fig. 82.) When the effective concentration of ions in a solution is equal to one gram ion in 1000 g. of water, the solution has unit activity. The reaction at this electrode is:

$$2\,H_3O^+ + 2\,\epsilon \rightleftharpoons H_2 + 2\,H_2O$$

This electrode is the primary reproducible standard reference electrode. Since there is no method of measuring its potential, it is arbitrarily assigned a zero potential, and the entire difference in potential between another electrode and the hydrogen electrode is attributed to the other electrode. Electrode potentials change with changes in concentration. *The standard electrode potential* of a metal is that difference in potential which it shows toward the standard hydrogen electrode in a solution of its ions at unit activity.

Metals which are more active than hydrogen give up electrons more readily than hydrogen and have a negative potential toward the hydrogen electrode. Metals that are less active have a positive potential. The electrode at which electrons are released by the reaction in the cell is called the *negative electrode*, and the electrode at which electrons are absorbed by ions in the solution is the *positive electrode*. The direction of the current is considered to be the direction of electron flow in the external circuit.

From the discussion in the preceding paragraph, it follows that the activities of the metals may be determined by measuring their standard electrode potentials. *The electromotive series of the metals is an arrangement in the order of decreasing standard electrode*
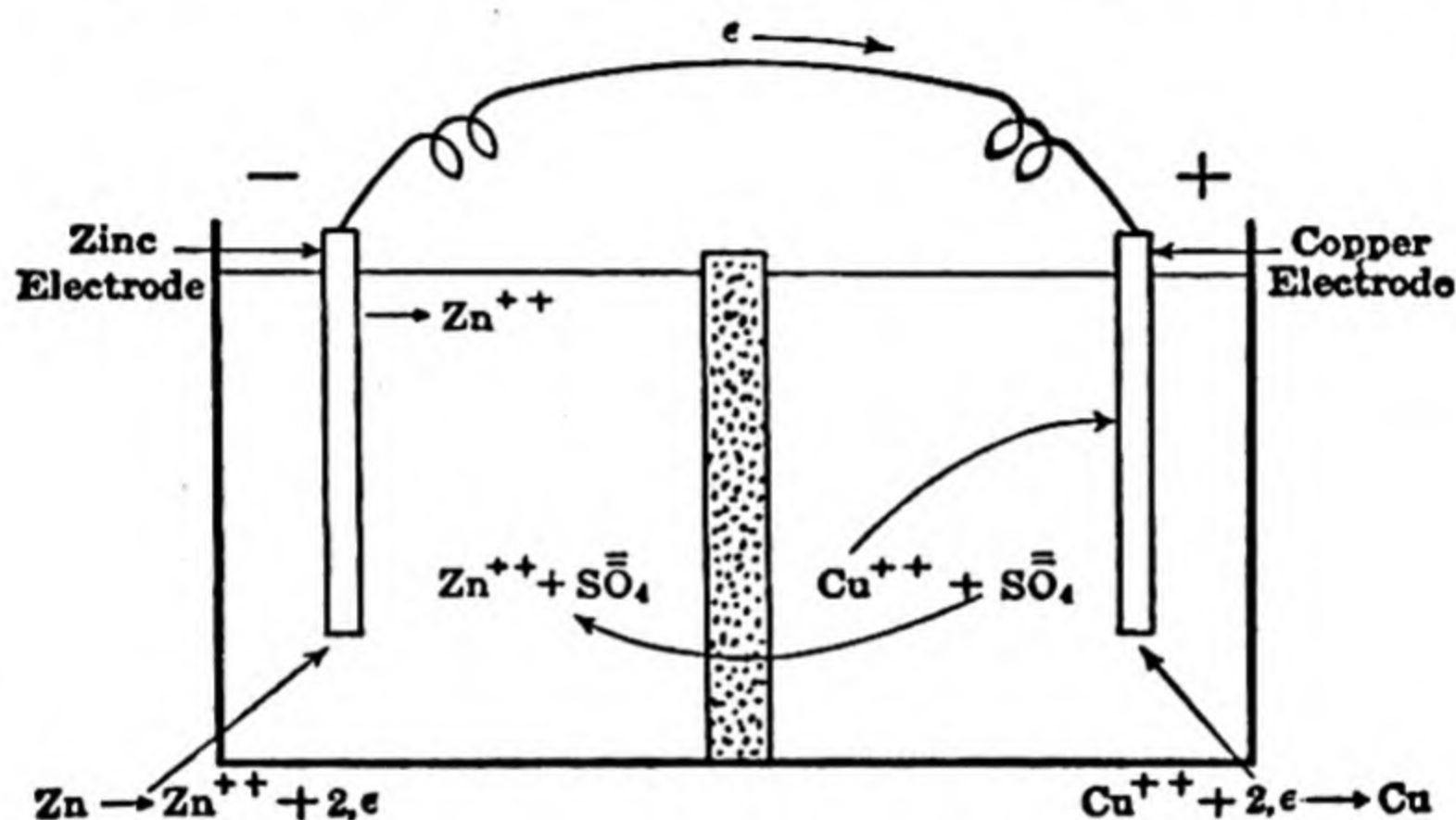
Fig. 83. Daniell Cell

potentials. (See Appendix, Table V.) Each metal in the list tends to displace the ions of those following it.

The Daniell Cell. This cell employs the displacement of cupric ions by zinc as the source of an electric current. The arrangement of the materials is shown diagrammatically in Fig. 83. The formation of zinc ions at the zinc electrode releases electrons, and a negative electrode potential is developed. The discharge of cupric ions at the copper electrode takes up electrons, developing a positive electrode potential. The solutions in the two compartments are maintained in practically the same electrical condition by the passage of ions through the walls of the porous cup. The difference in potential between the metal electrodes suffices to cause a stream of electrons to flow through the connecting wire.

The standard electrode potential of zinc at 25° is − 0.762 volt, and of copper + 0.345 volt. Since one of these potentials is positive and the other negative, the voltage of the cell is equal to the algebraic difference between the two electrode potentials.

$$E = 0.345 - (- 0.762) = 1.107 \text{ volts}$$

Zinc ions are formed in the solution about the zinc electrode, and copper is deposited on the copper electrode during the operation of this cell. Consequently, the only change in the materials in the cell is a change in the concentrations of the ions in solution. The electromotive force of the cell undergoes only small change.
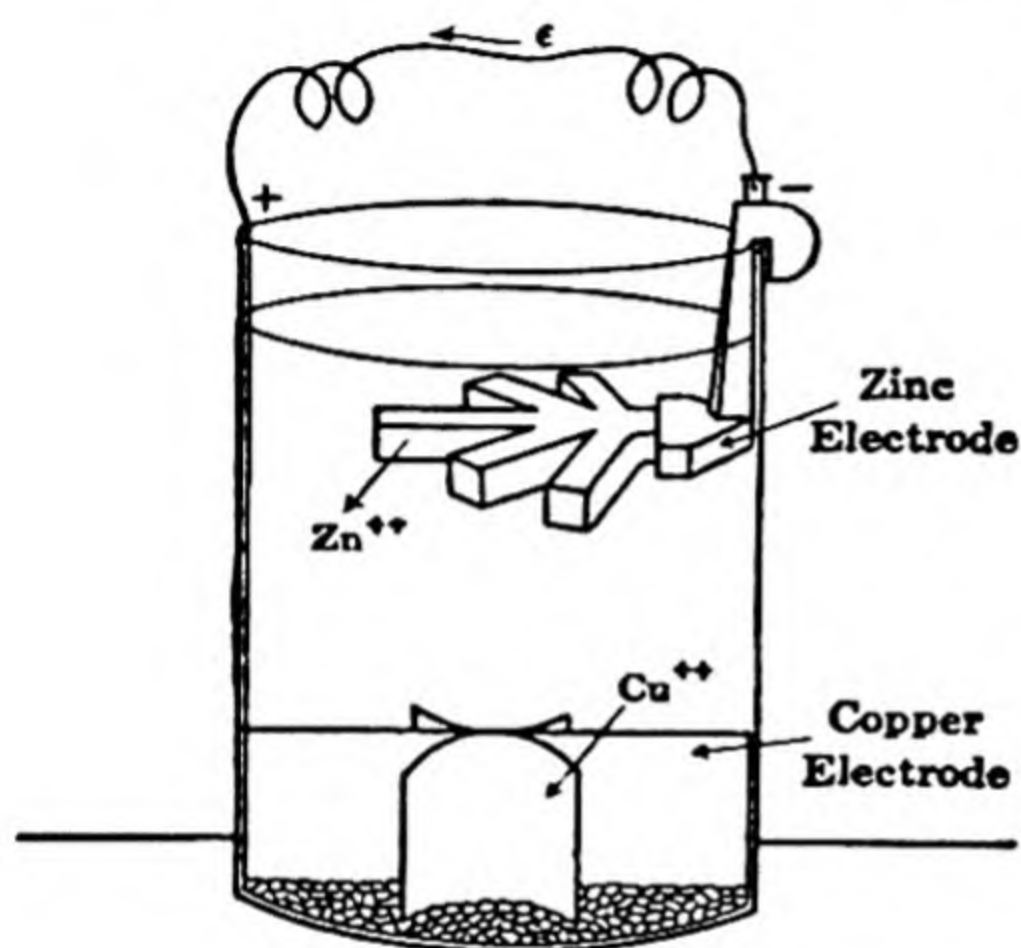
The same reaction may be carried out in the *gravity cell*, with the materials arranged as shown in Fig. 84. The copper electrode at the bottom of the battery jar is in a saturated solution of cupric sulfate, and an excess of solid cupric sulfate crystals is added to maintain saturation. The zinc electrode at the top of the jar is in a dilute solution of zinc sulfate. The difference in density aids in preventing the mixing of the solutions. During the operation of the cell, cupric ions travel toward the copper electrode at the bottom of the jar, and therefore the diffusion of these ions into the zinc salt solution takes place only very slowly. A covered copper wire leads up through the zinc sulfate solution to provide a connection for the external circuit.

Fig. 84. *Gravity Cell*
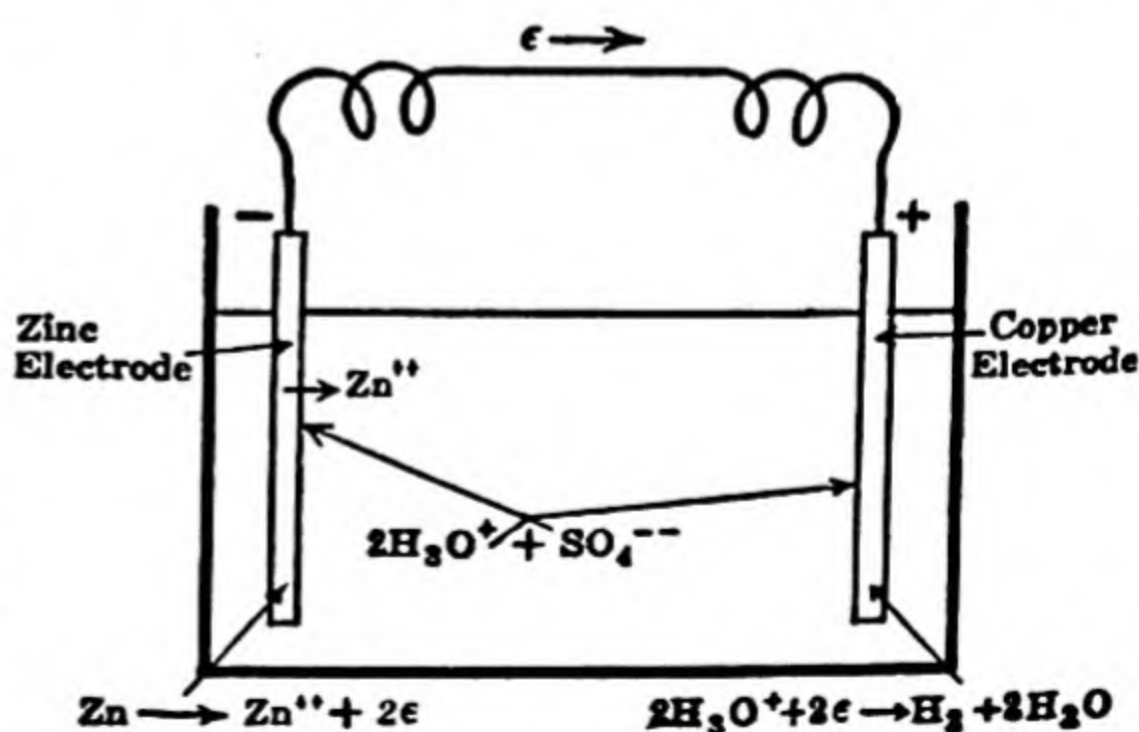
Fig. 85. *Simple Voltaic Cell*

Simple Voltaic Cells. Polarization. When zinc and copper electrodes are placed in dilute sulfuric acid and are connected

by an external conductor, a current flows through the circuit. (Fig. 85.) Zinc ions are formed at the surface of the zinc, releasing electrons and developing a negative electrode potential. Hydronium ions are discharged by the gain of electrons from the copper electrode, so that this electrode is positive. Positive ions are formed so rapidly and in such great numbers at the zinc electrode that a great excess of positive ions exists in the solution in immediate contact with this electrode. Hydronium ions, consequently, are discharged more readily at the copper electrode than at the surface of the zinc. In the solution as a whole, equivalent numbers of positive ions are present at all times, and the solution as a whole is electrically neutral.

A voltmeter in the circuit shows that there is a rapid drop in the voltage of the cell. This phenomenon is called *polarization*. It is due to the formation of molecular hydrogen at the surface of the copper electrode. The presence of this gas changes the chemical nature of the surface molecules of the electrode. This change causes a reverse potential, since hydrogen may form ions, liberating electrons with greater activity than copper. Thus, the voltage of the cell is reduced to the extent caused by this reverse potential.

Electric Couples. Corrosion. When pure zinc is placed in dilute sulfuric acid, little change can be observed. The displacement of hydrogen occurs uniformly at all points on the surface of the metal, and a film of the gas coats the metal, preventing contact with the acidic solution. If the zinc is impure, containing even small proportions of less active metals such as copper, the action proceeds rapidly. The two metals of different activity in contact with each other and with the acid constitute a minute voltaic cell. Hydrogen is now discharged at the surface of the inactive impurity, and does not coat the zinc nor prevent the action of the acid.

Pure iron is attacked only slowly by water containing dissolved electrolytes, but all of the commercial grades of iron are impure and contain carbon or metals of low activity. Impure iron corrodes rapidly in contact with solutions of electrolytes, the carbon or the metal of low activity serving as the inactive member of the couple. Tinned iron, tinplate, is an electric couple, tin being less active than iron. When tinplate is damaged so that there are perforations

through the tin coating, the iron rusts rapidly. Zinc is the more active of the two metals in galvanized iron. If the protective zinc coating over the iron is damaged, zinc is attacked by water containing dissolved electrolytes. The presence of carbon dioxide in water in contact with zinc causes the formation of the basic carbonate. This compound is insoluble so that it coats and protects the metal. The aluminum alloy, duralumin, contains metals which are less active than aluminum, and it is subject to corrosion. *Alclad sheet* consists of an aluminum alloy coated with a thin layer of pure aluminum. This material is not subject to rapid corrosion, because the aluminum of the outer layer becomes coated with a protective film of the slightly active aluminum oxide.
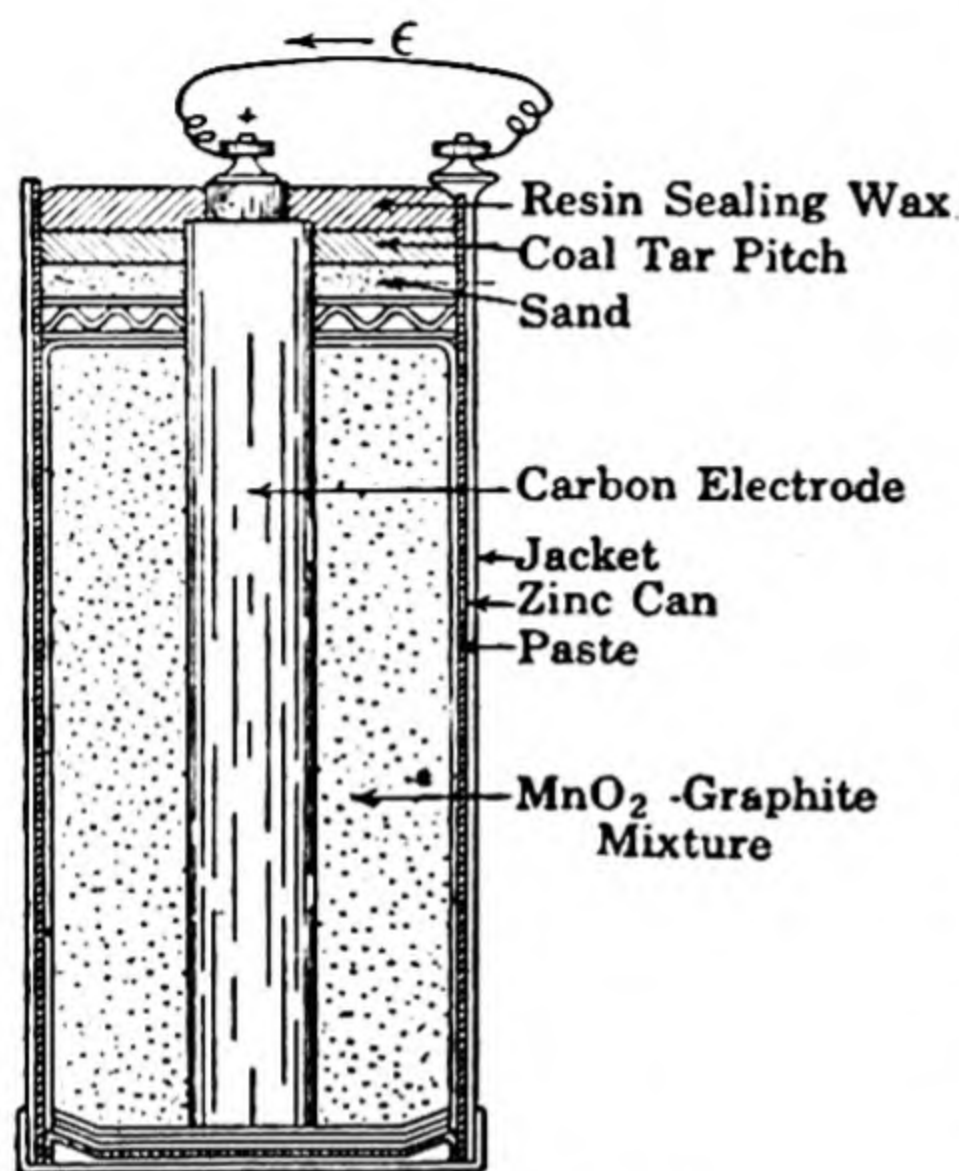
The Dry Cell. A Depolarizing Cell. The Daniell cell and the simple voltaic cell illustrate the arrangement of the materials required for the production of electric current by displacement reactions. The gravity cell is still in use to a limited extent, but is no longer commercially important. The best known of the electric cells in general use is the dry cell shown in Fig. 86. This cell employs the displacement of ammonium ions by zinc as source of electrical energy.

Fig. 86. Dry Cell

$$Zn \longrightarrow Zn^{++} + 2\epsilon$$
$$2NH_4^+ + 2\epsilon \longrightarrow 2NH_3 + H_2$$
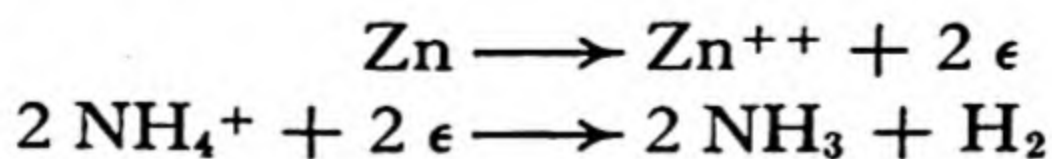
The ammonia produced in this reaction is absorbed in the water in the cell and reacts with zinc ions to form complex ions. Hydrogen causes polarization, and manganese dioxide is packed about the carbon electrode to oxidize hydrogen to water and thus depolarize the cell during periods of rest.

$$2MnO_2 + H_2 \longrightarrow Mn_2O_3 + H_2O$$
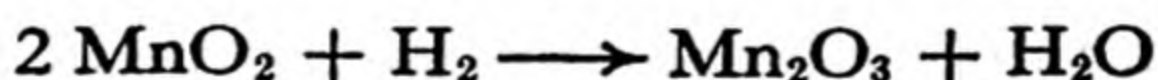
Graphite is mixed with manganese dioxide to decrease the resistance of the cell. The outer container is made of zinc and is itself the active electrode. A thick layer of absorbent paper serves as a liner to separate the graphite and manganese dioxide mixture from the metallic zinc. A narrow space between the liner and the zinc can is filled with a flour paste containing some of the electrolytic substances. In some of the cells, especially those made for flashlights, the liner is eliminated and the paste itself separates the graphite mixture from the zinc. The cell is sealed with pitch to prevent the evaporation of the water absorbed by the porous contents of the cell. The voltage of this cell is about 1.5.

Voltage and Amperage of Cells. All of the cells described thus far are *primary cells*. The substances required for the reaction are placed directly in the primary cells. When any one of these substances has reacted completely, the activity of the cell is terminated until this substance has been replenished. The electromotive force developed by a cell is dependent on the nature of the substances of which the cell is constructed and is affected also by the concentrations of the substances and the temperature. Higher potentials may be secured by connecting a number of cells in series, thus multiplying the effect. The capacity of a cell depends on the amount of the reacting substances, capable of undergoing oxidation-reduction. Large cells, containing large quantities of substances, furnish greater amounts of electricity but do not develop higher potentials than small cells containing the same materials. A cell produces 96,500 coulombs of electricity for each gram equivalent weight of the substance oxidized at one electrode, with the corresponding reduction of another substance at the other electrode. The amperage of a cell depends on the rate at which the reactions occur, while the voltage depends on the activity of the reactants.

The Lead Storage Cell. The reactions occurring in primary cells lead to the formation of reduction products at one electrode and oxidation products at the other. In some instances, it is possible to reverse these reactions by the passage of a direct current of electricity through the cell, thus restoring the active materials by electrolysis. The ordinary *storage cell*, the lead accumulator, used in batteries for automobiles, is constructed of materials suitable

for repeated reverse changes. The electrodes are gratings of lead containing 5–12 per cent of antimony. Antimony gives a better casting and adds mechanical strength but increases the resistance. One plate is coated with finely divided spongy lead and the other with lead dioxide. The cell is filled with sulfuric acid diluted to a specific gravity of about 1.2.

During the discharge of this cell (Fig. 87), electrical energy is produced as in other primary cells, by the reactions that occur at the
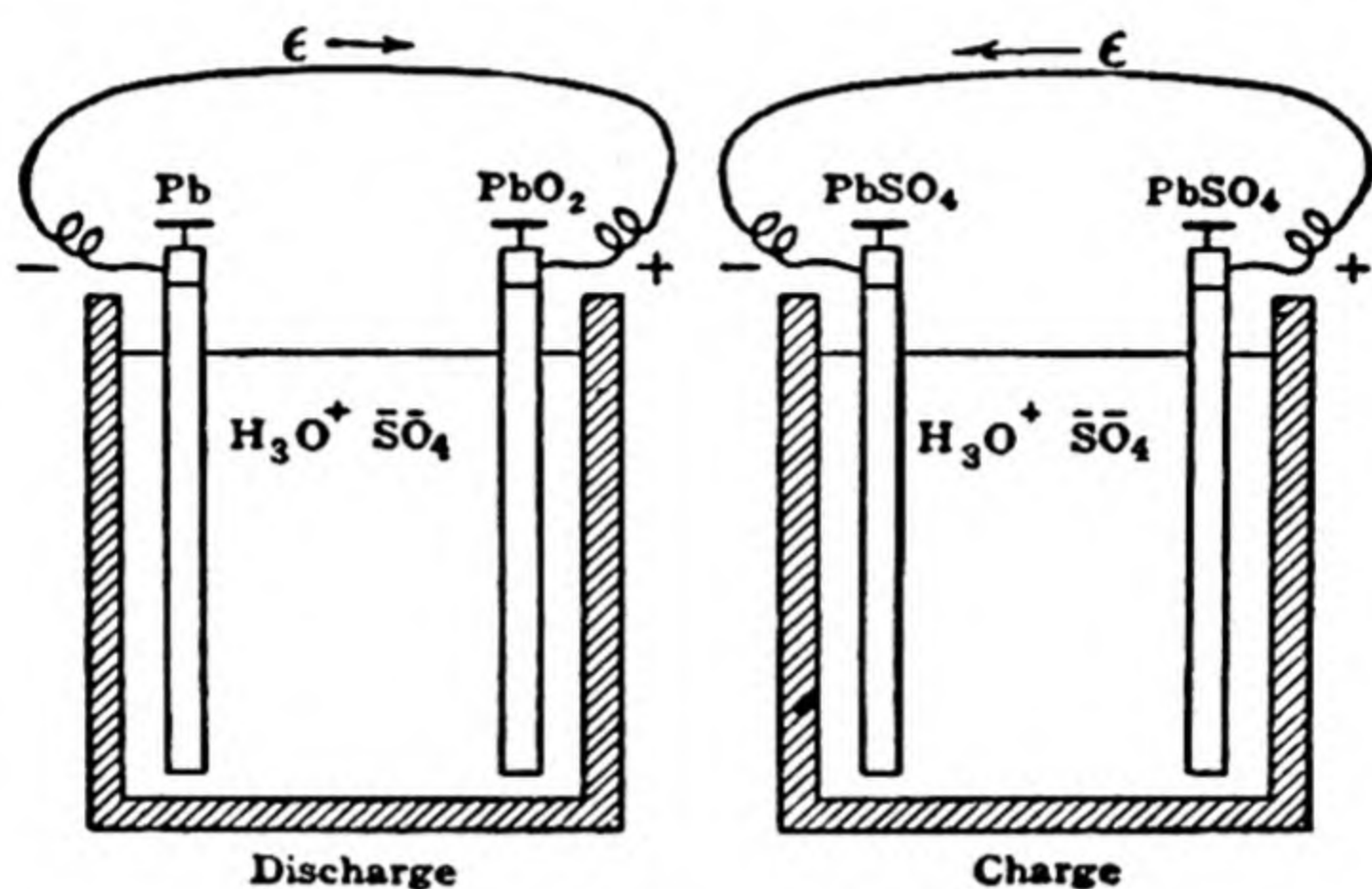
Fig. 87. Storage Cell

electrodes. The oxidation of lead in the presence of sulfate ions produces lead sulfate, and the electrode becomes negatively charged by the liberation of electrons.

$$Pb + SO_4^{--} \longrightarrow PbSO_4 + 2\,\epsilon$$
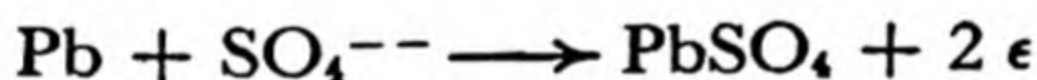
The reduction of lead dioxide occurs at the other electrode. The oxidation number of lead is 4 + in the dioxide, but this oxidation number is not an electrovalence. The reaction involves the interaction of lead dioxide with hydronium and sulfate ions to form lead sulfate and water in a reaction requiring a supply of electrons. Although there are several probable intermediate steps in the reaction, the changes at this electrode may be summarized by a single ion-electron equation.

$$PbO_2 + 4\,H_3O^+ + SO_4^{--} + 2\,\epsilon \longrightarrow PbSO_4 + 6\,H_2O$$
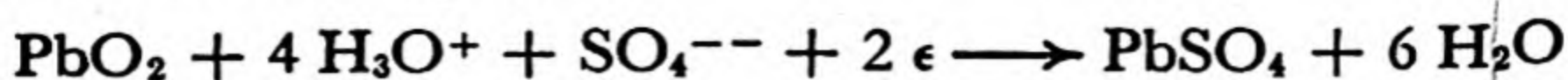
A single equation combining these two reactions may be obtained by adding the partial equations, but the operation of the cell

requires that the two partial reactions occur at different places, not as a single reaction.

$$Pb + PbO_2 + 4 H_3O^+ + 2 SO_4^{--} \longrightarrow 2 PbSO_4 + 6 H_2O$$

Lead sulfate is insoluble and adheres to the plates. Sulfuric acid enters into the reaction at each electrode, and the density of the solution decreases. During the discharge of the cell, the two electrodes approach the same composition, and the voltage of the cell falls.

During the charging of the cell (Fig. 87), a direct current of electricity, flowing in the direction opposite to that of the discharge, is passed through the cell. The electrodes retain the same sign toward each other, but electrons now enter the cell at the negative electrode, whereas they leave the cell at this electrode during discharge. At the cathode, lead sulfate is reduced to finely divided lead, which adheres to the plate, and sulfate ions are released to the solution.

$$PbSO_4 + 2 \epsilon \longrightarrow Pb + SO_4^{--}$$
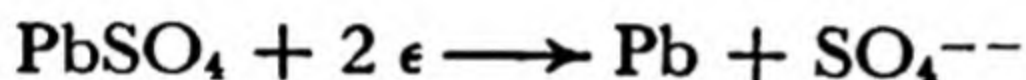
At the anode, lead sulfate is oxidized to lead dioxide, producing hydronium and sulfate ions in the solution.

$$PbSO_4 + 6 H_2O \longrightarrow PbO_2 + 4 H_3O^+ + SO_4^{--} + 2 \epsilon$$
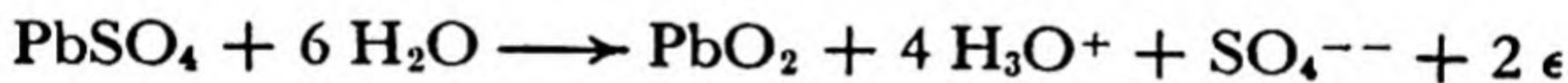
The density of the solution increases during the charging of the cell, and the condition of the cell may be determined by measuring the specific gravity of the cell liquid. The charged cell has a voltage of about 2.2. When the voltage has dropped to 1.9 and the specific gravity of the acid to 1.05, the cell should be recharged. Hydrogen and oxygen are evolved to some extent during the charging of the cell, and it is necessary from time to time to add distilled water to the cell. The efficiency of the cell is about 75 per cent.

EXERCISES

1. Define oxidation-reduction in terms of electronic changes.
2. What is an ion-electron equation? Write ion-electron equations for each half reaction in the following displacements, and derive the complete equation on the basis of these partial equations: (*a*) $Zn + Hg_2(NO_3)_2$; (*b*) $Al + HgSO_4$; (*c*) $Zn + BiCl_3$; (*d*) $Cl_2 + Na_2S$.
3. What is meant by electrolysis?
4. Describe the electrolysis of the following solutions. Draw diagrams to indicate

the arrangement of the materials in the cell and the ion migration. Write ion-electron equations for the half reactions at the anode and cathode in each instance: (a) $CuSO_4$; (b) $HgCl_2$; (c) CdI_2; (d) KCl; (e) Na_2SO_4.

5. What conditions must be established in order to secure an electric current from the energy evolved during an oxidation-reduction reaction?

6. What is meant by standard electrode potential? Upon what factors does the voltage of a cell depend?

7. Draw diagrams to show the arrangement of the materials necessary to obtain an electric current from the following oxidation-reduction reactions, and write ion-electron equations for the reactions at the electrodes in each cell. (a) $Zn + Ag_2SO_4$; (b) $Zn + SnCl_2$; (c) $Zn + CuSO_4$; (d) $Zn + NH_4Cl$; (e) $Cu + HgSO_4$; (f) $FeCl_2 + Cl_2$.

8. Explain why iron containing carbon corrodes more rapidly than pure iron.

9. What is meant by polarization? Why is the Daniell cell a nonpolarizing cell? What is the function of manganese dioxide in the dry cell?

10. Explain the action of a storage cell during (a) discharge and (b) charge.

SUPPLEMENTARY READINGS

Creighton, H. J., and W. A. Koehler, *Electrochemistry*, John Wiley & Sons, Inc., New York, 1935, Vol. II, chaps. II–IV, VI.

Getman, F. H., and F. Daniels, *Outlines of Theoretical Chemistry*, John Wiley & Sons, Inc., New York, 1943, chaps. XV–XVI.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, American Book Company, New York, 1936, chap. XIV.

Hammett, L. P., *Solutions of Electrolytes*, McGraw-Hill Book Company, Inc., New York, 1936, chap. VII.

Newell, L. C., "Faraday's Contributions to Chemistry," *J. Chem. Education* 8, 1493 (1931).

Chapter 16

COMPLETED IONIC REACTIONS

Double decomposition reactions involve an exchange in the corresponding parts of the reacting substances. These reactions in solutions of electrolytes are ionic in nature. If one or more of the reacting substances is a weak electrolyte, the reaction involves the dissociation of such substances into ions and the reassociation of the ions to form the products. In solutions of strong electrolytes, the substances are ionic in the separate solutions, so that when the solutions are mixed, the essential reaction is the association of ions forming molecular products or ionic solids such as salts.

If dilute solutions of two strong electrolytes that do not contain an ion in common are mixed, the resulting solution contains two varieties of positive ions and two varieties of negative ions. The nature of the substances formed by the interaction of these ions determines whether or not a reaction will occur. If the possible products are soluble strong electrolytes and no changes in oxidation numbers occur, all of the ions can remain together in solution without reaction. Thus, dilute solutions of potassium chloride and sodium nitrate may be mixed without reaction, because the four possible compounds formed by the association of the ions in the solution are strong electrolytes. The conclusion that no reaction occurs between these substances in dilute solution is confirmed by the fact that no change in temperature can be detected when the solutions are mixed.

Completed Ionic Reactions. The general condition required for double decomposition reactions between electrolytes is that ions be removed from the solution. Ions may be removed from solution by the formation of slightly soluble solids, weak electrolytes in solution, or slightly soluble gases. Most of these reactions are reversible and lead to a state of equilibrium. The extent of reaction, therefore, depends on the proportions of the substances

that may remain in solution at equilibrium. If the concentrations of the ions of the reacting substances at equilibrium are insignificantly small, the reaction is called a *completed ionic reaction*. Usually, such reactions are not complete in the strict sense, and many of them may be reversed by changing conditions such as the temperature and the concentrations of other varieties of ions in the solution.

Precipitation of Solids. The formation of a product that is only slightly soluble under the conditions of the experiment leads to the elimination of its ions from the solution and causes the reaction to proceed practically to completion. Many of the substances formed by precipitation are *ionic solids*, but others are *molecular products*. The precipitated ionic solid is assumed to be in direct equilibrium with its ions, but the molecular solid is in equilibrium with the dissolved molecular substance which is, in turn, in equilibrium with its ions. In both types, only low concentrations of the ions of the slightly soluble product may remain in solution.

Slightly soluble salts are precipitated by the reaction of solutions that furnish the necessary ions in sufficiently high concentrations. Lead chloride may be precipitated by the reaction of solutions of lead nitrate and sodium chloride. The ionic equation for this reaction may be written in the form:

$$Pb^{++} + 2\,NO_3^- + 2\,Na^+ + 2\,Cl^- \rightleftharpoons PbCl_2 \downarrow + 2\,Na^+ + 2\,NO_3^-$$
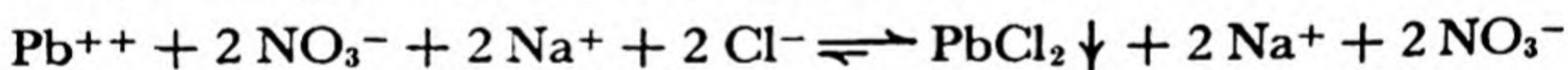
Since sodium and nitrate ions remain free in the solution, it is evident that they do not enter into the reaction. They are, therefore, omitted from the ionic equation.

$$Pb^{++} + 2\,Cl^- \rightleftharpoons PbCl_2 \downarrow$$
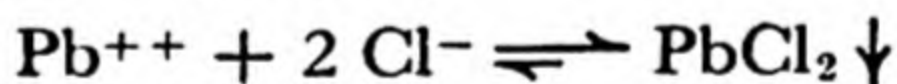
The presence of both lead and chloride ions in solution in equilibrium with the precipitate may be demonstrated by direct test. The suspension is filtered to remove the precipitate, and the filtrate is divided into two portions. The addition of nitric acid and silver nitrate to one portion causes the formation of a white precipitate of silver chloride, which is less soluble than lead chloride.

$$Ag^+ + Cl^- \rightleftharpoons AgCl \downarrow$$
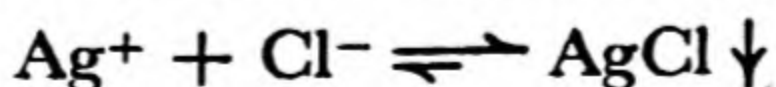
The addition of potassium chromate to the other portion of the filtrate produces a yellow precipitate of lead chromate.

$$Pb^{++} + CrO_4^{--} \rightleftharpoons PbCrO_4 \downarrow$$
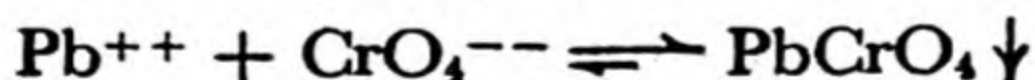
Ionic reactions are nearly complete if the formation of a precipitate reduces the concentrations of its ions to an insignificant value.

Molecular solids, such as some of the weak acids, may be precipitated by the reaction of a strong acid with a solution of a salt that furnishes the anions of this acid. Thus, boric acid, H_3BO_3, is a weak acid, only moderately soluble at room temperature. The addition of sulfuric acid to a solution containing borate ions causes the formation of the molecular acid in solution. If the concentrations are great enough, a precipitate is formed. Hence, two equilibria are involved in the suspension of this acid in its saturated solution.

$$3\,H^+ + BO_3^{---} \rightleftharpoons H_3BO_3 \text{ in solution} \rightleftharpoons H_3BO_3 \downarrow$$

The final result is similar to that in the precipitation of the ionic solid, and *the reaction is virtually complete if the concentration of the ions in the equilibrium mixture is small.*

Summary of Solubilities. Solubility is usually defined as the weight of the solute in a definite weight of a specific solvent at a specified temperature. The solubilities of a number of substances in water are shown in the Appendix, Table VIII. It is impractical to commit specific solubility data to memory, but a general understanding of solubility relationships is necessary for the selection of substances for use in chemical reactions. The statements in the following summary of solubilities are qualitative and are applicable only to the common salts in each group. The word insoluble is used in the previously discussed sense: practically insoluble.

Acids. The common strong acids are soluble and are highly ionized. Weak acids are only slightly ionized.

Basic Hydroxides. The hydroxides of sodium and potassium are highly soluble; those of barium, strontium, and calcium moderately soluble; and the other common metal hydroxides have low solubility.

Salts. Soluble salts in general are ionic in solution. Mercuric chloride, mercuric cyanide, and lead acetate are soluble but yield only low concentrations of their respective cations.

Sodium and potassium salts of the common acids are soluble.

Nitrates, chlorates, and acetates are soluble.

Chlorides, bromides, and iodides are soluble, except silver, lead, mercurous, and cuprous halides and mercuric iodide.

Sulfates, except those of barium, strontium, and lead, are soluble, but calcium sulfate and silver sulfate have low solubility.

Sulfides of sodium, potassium, and ammonium are soluble. The other sulfides have low solubility, but the concentration of sulfide ions in aqueous solution is not great enough to cause the precipitation of the sulfides of a number of common metals, *e.g.*, magnesium, calcium, barium, strontium, and aluminum.

Carbonates, phosphates, and silicates of sodium and potassium are soluble, and ammonium carbonate and ammonium phosphate are soluble salts.

The Solubility Product Principle. Since the concentrations of the ions of a slightly soluble salt in its saturated solution are low, the average distances between the ions are relatively great. The forces of interionic attraction have little effect on the activities of the ions under these conditions, and only small errors are introduced if it is assumed that the molar concentrations of the ions actually represent their activities. A state of equilibrium exists between the crystalline solid and its ions in a saturated solution of a salt containing an excess of the solid. The surface of the solid is the active area in the exchange of ions, and the surface effect is constant at equilibrium. Hence, the application of the law of molecular concentration or mass action to the system involving silver chloride and its ions gives the relation:

$$\frac{[Ag^+] \times [Cl^-]}{a\ constant} = K$$

or

$$[Ag^+] \times [Cl^-] = K \times a\ constant$$

This product is itself a constant, frequently designated by the letter S, with which the formula of the salt may be written to identify the particular system to which the constant applies.

$$[Ag^+] \times [Cl^-] = S_{AgCl}$$

This product, known as *the solubility product or ion concentration product*, is numerically equal to the product of the molar concentrations of

the ions in a saturated solution of a slightly soluble strong electrolyte, with each concentration raised to the power shown by the coefficient of the ion in the equilibrium equation. The solubility product expression for lead chloride is:

$$[Pb^{++}] \times [Cl^-]^2 = S_{PbCl_2}$$

If the concentration of one of the ions involved is greater than the equivalent proportion, the concentration of the other is correspondingly less.

The solubility products of most substances increase with rise in temperature, but there is no regularity in the rate of increase for different solutes. The solubility product is also affected by changes in the nature of the solvent. The addition of other solutes, which do not have an ion in common, changes the solvent from pure water to a salt solution. The solubility product increases somewhat as the total concentration of ions in the solution increases. This change is small in dilute solutions. The solubility product principle is important in the treatment of the equilibria involved in the precipitation of slightly soluble electrolytes.

The solubility product of a substance is easily calculated from solubility data. The solubility of lead chloride, for example, is 0.993 g. in 100 g. of water. First, the molal concentration is calculated by dividing the number of grams of lead chloride in 1000 g. of water by the number of grams in one mole.

$$9.93 \div 278.12 = 0.0357 \text{ mole}$$

The molar concentration is practically the same as the molal concentration in solutions of this dilution. From the equilibrium equation,

$$PbCl_2 \downarrow \rightleftharpoons Pb^{++} + 2\ Cl^-$$
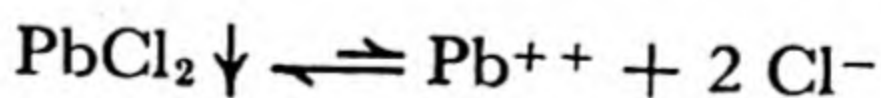
it follows that the concentration of the lead ion is 0.0357 molar, and that the concentration of the chloride ion is $0.0357 \times 2 = 0.0714$ molar. The solubility product of lead chloride is:

$$[Pb^{++}] \times [Cl^-]^2 = S_{PbCl_2}$$
$$0.0357 \times 0.0714^2 = 1.8 \times 10^{-4} \text{ at } 20°$$

The solubility of a slightly soluble strong electrolyte may be calculated from its solubility product, assuming that the forces

of interionic attraction are insignificant. The solubility product * of silver chloride at 20° is 1.1×10^{-10}. The molar concentrations of the silver and chloride ions in a suspension of silver chloride in water are equal, and each is equal to the molar concentration of the salt in its saturated solution.

$$AgCl \downarrow \rightleftharpoons Ag^+ + Cl^-$$
$$[Ag^+] \times [Cl^-] = S_{AgCl} = 1.1 \times 10^{-10}$$
$$[Ag^+] = [Cl^-] = \sqrt{1.1 \times 10^{-10}} = 1.04 \times 10^{-5}$$

The solubility of silver chloride is equal to 1.04×10^{-5} moles per liter. The solubility in grams per liter is:

$$1.04 \times 10^{-5} \times 143.34 \text{ g.} = 0.0014 \text{ g.}$$

The formation of a precipitate is caused by mixing solutions that furnish greater concentrations of ions than equilibrium permits. The maximum concentrations of ions which may exist together in equilibrium are defined by the solubility product of the substance. The solubility of barium sulfate is small.

$$[Ba^{++}] \times [SO_4^{--}] = S_{BaSO_4} = 1 \times 10^{-10}$$

Solutions of barium chloride and a soluble sulfate may contain relatively high concentrations of the barium and sulfate ions. When these solutions are mixed, precipitation occurs because the condition represented by the expression

$$[Ba^{++}] \times [SO_4^{--}] > S_{BaSO_4}$$

cannot exist in solution at equilibrium. In general, a slightly soluble electrolyte may be precipitated by mixing solutions containing the appropriate ions in concentrations that give a product greater than the solubility product of the substance.

The dissolving of a precipitate requires maintaining conditions under which the ion concentrations are less than those expressed by the solubility product relationship. Ion concentrations may be reduced by *adding further quantities of the solvent.* Consequently, a greater quantity of the solute may be held in solution, bringing its concentration to the value in the smaller volume. This method is of no practical importance in dissolving a substance, unless the

* The solubility products of a number of common substances are tabulated in the Appendix, Table IX.

substance is at least moderately soluble. The solubility product of barium sulfate is 1×10^{-10} at 20°, and one liter of the saturated solution contains only 1×10^{-5} moles of this solute. Hence, 100,000 liters of water would be required to dissolve one mole, or approximately 428 liters to dissolve one gram of barium sulfate.

A second method of dissolving precipitates is based on the increased solubility of many solutes at higher temperatures. This procedure has practical application for those precipitates that are among the more soluble of the slightly soluble substances, and that are much more soluble at high than at low temperatures. If a suspension of lead chloride in water is heated to the boiling point, a much greater weight of the solid may be dissolved by the same quantity of water. The solubility product of lead chloride increases greatly with rise in temperature.

$$S_{PbCl_2} \text{ at } 20° < S_{PbCl_2} \text{ at } 100°$$

Therefore, the concentrations of lead and chloride ions present in the saturated solution at 20° are far below the equilibrium concentrations for the higher temperature. Hence, the precipitated lead chloride may be dissolved completely at the boiling temperature, unless indeed the quantity is greater than required to produce a saturated solution even at this higher temperature.

The method commonly used to dissolve slightly soluble solids involves chemical reactions by which soluble products are formed. This may be accomplished by the addition of reagents, which cause a reduction in the concentration of one variety of ion in equilibrium with the precipitate. The actual ion concentration product is thus made less than the solubility product constant. Many precipitates are dissolved by the formation of slightly soluble weak electrolytes. Magnesium hydroxide has low solubility.

$$Mg(OH)_2 \downarrow \rightleftharpoons Mg^{++} + 2\,OH^-$$
$$[Mg^{++}] \times [OH]^2 = S_{Mg(OH)_2} = 2.8 \times 10^{-11}$$
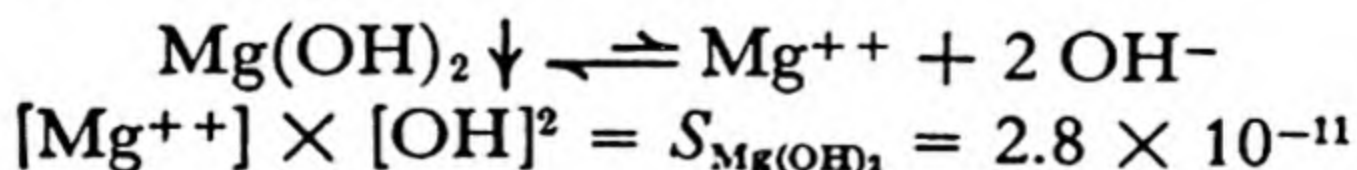
When an excess of hydrochloric acid is added, the concentration of the hydroxide ion is greatly reduced.

$$H^+ + OH^- \rightleftharpoons H_2O$$
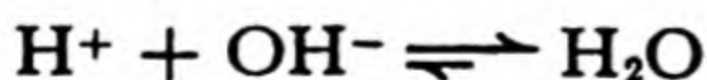
This reduction in the concentration of the hydroxide ion destroys the equilibrium between solid magnesium hydroxide and its ions.

$$[Mg^{++}] \times [OH]^2 < 2.8 \times 10^{-11}$$

Consequently, magnesium hydroxide is dissolved by reaction with hydrochloric acid, producing soluble magnesium chloride.

$$Mg(OH)_2 \downarrow + 2\,H^+ \longrightarrow Mg^{++} + 2\,H_2O$$
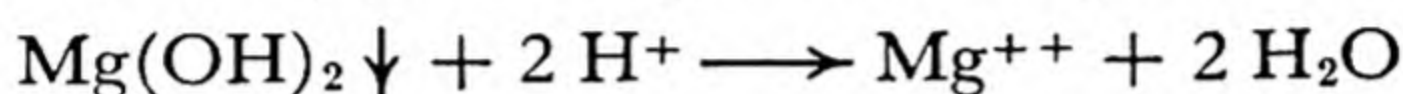
Slightly soluble salts of many of the acids may be dissolved by reaction with strong acids. The concentration of the anion of the salt is reduced by the formation of weak acid in molecular state. Calcium carbonate may be dissolved by reaction with hydrochloric acid. When this salt is suspended in water,

$$CaCO_3 \downarrow \rightleftharpoons Ca^{++} + CO_3^{--}$$
$$[Ca^{++}] \times [CO_3^{--}] = S_{CaCO_3} = 2 \times 10^{-8}$$
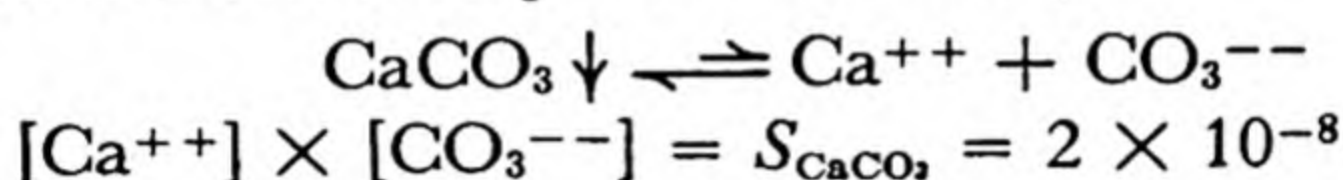
Carbonate ions are removed from the solution by reaction with the hydrogen ions of the acid with the formation of carbon dioxide gas.

$$CO_3^{--} + 2\,H^+ \longrightarrow H_2O + CO_2 \uparrow$$
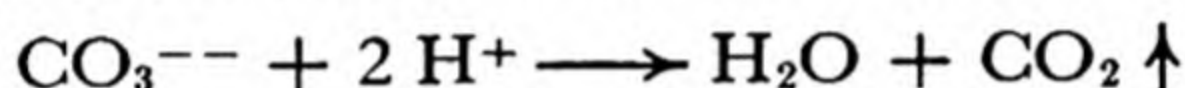
The ion concentrations are now too low for equilibrium with the solid, and the precipitate dissolves with the production of a soluble calcium salt.

$$[Ca^{++}] \times [CO_3^{--}] < 2 \times 10^{-8}$$
$$CaCO_3 \downarrow + 2\,H^+ \longrightarrow Ca^{++} + H_2O + CO_2$$
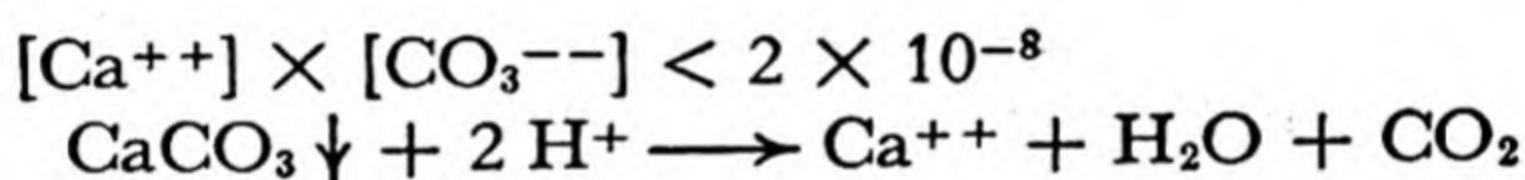
Formation of Weak Electrolytes in Solution. The reaction of a strong acid with a soluble salt of a weak acid leads to the formation of the weak acid in the molecular state, and causes the reaction to proceed nearly to completion. The reaction of hydrochloric acid with sodium acetate produces molecular acetic acid. Only low concentrations of hydrogen and acetate ions may remain together in solution. Sodium and chloride ions undergo no significant change.

$$H^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2$$
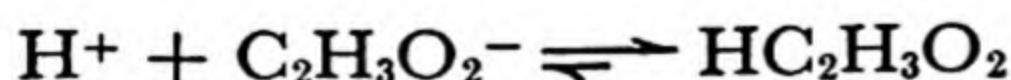
This equation represents the ionic equilibria for solutions of acetic acid, discussed on page 223. Hence, the extent of the reaction depends on the concentrations of these ions, which may exist together at equilibrium. The concentration relationships are shown by the ionization constant of the acid.

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

The numerical value of the ratio required for equilibrium is affected to only a small degree by the presence of sodium and chloride ions in the solution.

In a similar manner, salts of weakly basic substances react with highly ionized bases. The formation of the molecular weak base reduces the concentrations of its ions to the value permitted by the ionic equilibria of the weak base. A solution of sodium hydroxide reacts with ammonium chloride to form ammonia, a weak base.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$
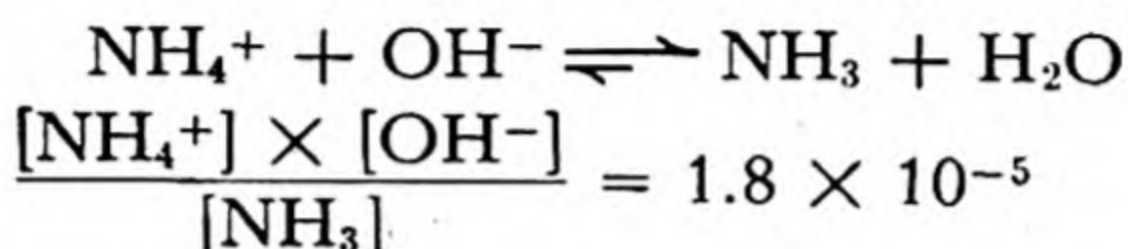
The reaction of acids with metal hydroxides is a virtually completed reaction because of the low degree of ionization of water. Hydrochloric acid and sodium hydroxide are strong electrolytes. When solutions containing equivalent quantities of these substances are mixed, the concentrations of the hydrogen and hydroxide ions are much greater than required for equilibrium with molecular water. Therefore the ions unite, leaving sodium and chloride ions in solution, i.e., a solution of sodium chloride.

$$H^+ + OH^- \rightleftharpoons H_2O$$
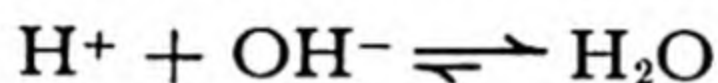
Ionic reactions are practically complete if the formation of a molecular product in solution reduces the concentrations of its ions to an insignificant value.

Formation of a Slightly Soluble Gas. The formation of a slightly soluble molecular product, or one which decomposes under the conditions of the experiment, is an additional factor that affects the extent of ionic reactions. The formation of an insoluble, weakly ionized solid has been discussed as one type of precipitation reaction. If a gaseous product escapes from solution, or is driven out by the application of heat, equilibrium is destroyed, and the reaction resulting in this product is completed. If an atmosphere of the gas is maintained in contact with the liquid in which it is soluble, the concentration of the dissolved substance depends on its solubility under existing conditions of temperature and pressure. The reaction of hydrochloric acid with sodium sulfide produces hydrogen sulfide, which is both slightly ionized and slightly soluble. The other product is a strong electrolyte, which has no significant effect on the ionic equilibria for hydrogen sulfide. In a closed

container, an atmosphere of the gas is maintained above the liquid, and equilibrium is established. Nevertheless, the concentrations of the ions at equilibrium are small.

$$2\,H^+ + S^{--} \rightleftharpoons H_2S \text{ (dissolved)} \rightleftharpoons H_2S \text{ (gas)}$$
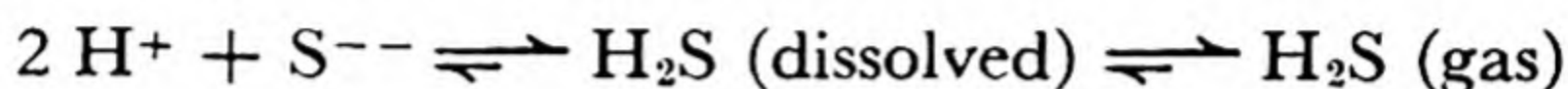
The ionic equilibria for hydrogen sulfide are described by the ionization constant.

$$\frac{[H^+]^2 \times [S^{--}]}{[H_2S]} = K_{H_2S} = 1 \times 10^{-22}\ (20°)$$

The concentration of hydrogen sulfide in its saturated solution at 20° and a pressure of the gas equal to one atmosphere is approximately 0.1 M. Therefore, the equilibrium concentrations for the ions in the saturated solution are shown by the constant:

$$[H^+]^2 \times [S^{--}] = 1 \times 10^{-22} \times 0.1 = 1 \times 10^{-23}\ (20°)$$

Ionic reactions are practically complete if they produce an insoluble gas. If the container is open so that the hydrogen sulfide gas escapes, equilibrium conditions are not maintained, and the reaction is completed.

$$2\,H^+ + S^{--} \longrightarrow H_2S \uparrow$$
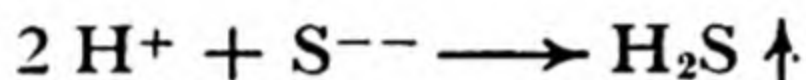
In a number of instances the product of a reaction is unstable toward heat so that it decomposes at the temperature of the reaction. Such reactions are similar in principle to the types already discussed. The reaction of hydrochloric acid with a soluble carbonate produces weakly ionized carbonic acid as the direct product, but this substance decomposes at room temperature with the formation of gaseous carbon dioxide. Equilibrium results if an atmosphere of the gas is maintained in contact with the liquid, but the concentrations of the ions permitted at equilibrium are small.

$$2\,H^+ + CO_3^{--} \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$
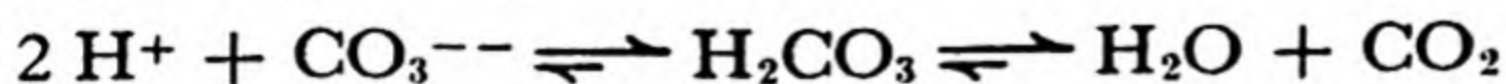
The concentration of the dissolved carbon dioxide at fixed temperature varies with the pressure of the gas.

$$2\,H^+ + CO_3^{--} \rightleftharpoons H_2O + CO_2 \text{ (dissolved)} \rightleftharpoons CO_2 \uparrow$$
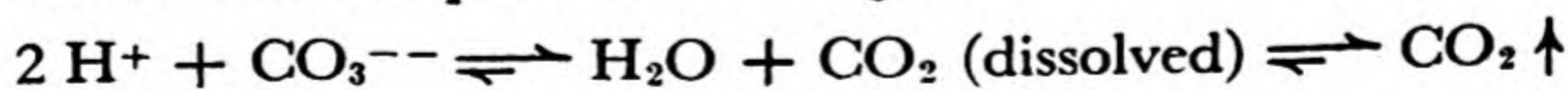
However, if carbon dioxide escapes continuously from the solution, equilibrium conditions are not maintained.

$$2\,H^+ + CO_3^{--} \longrightarrow H_2O + CO_2 \uparrow$$
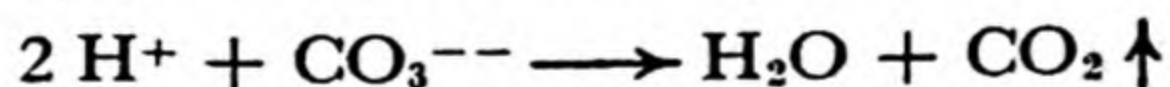
Formation of Complex Ions. There are a number of ions, known as complex ions, which are formed by the union of two or more simple ions or by the union of simple ions and molecules. The ions in aqueous solutions are commonly hydrated and, hence, are complex ions. The hydronium ion, H_3O^+, is a complex ion formed by the combination of a proton with a water molecule. Ions formed by the addition of molecules of the solvent are a special variety of complex ion, called solvated ions. In experimental practice, a complex ion is one the formation of which causes the more or less complete removal of the simple ions from the solution. The stability of a complex ion is measured by the concentrations of its decomposition products required for equilibrium. The smaller the concentrations of the simple products at equilibrium, the greater is the stability of the complex ion.

The combination of simple ions with other ions and with molecules is not in accord with the oxidation numbers of the substances involved. Thus, the cupric ion may add four molecules of water or four molecules of ammonia without change in its electrovalence. A secondary valence relationship is involved in the formation of these complex products. Werner called this the *coordination number*. It is equal to the number of atoms or radicals that a central atom tends to hold in combination. The coordination number is 4 in many of the more familiar complex ions, but 6 is also common. The number is always even and varies from 2 to 12, but a specific ion tends to retain a constant coordination number. The cadmium ion, for example, holds in combination four atoms or radicals, *e.g.*, $CdCl_4^{--}$, $Cd(CN)_4^{--}$, $Cd(NH_3)_4^{++}$, and $Cd(H_2O)_4^{++}$.

The formation of complex ions is attributed to the sharing of electrons between the constituent parts. The electron bond is of the coordinate type in which both of the electrons in the pair originate from the same atom or ion. Molecules and ions, which readily add in this manner to other ions, contain atoms that have unshared electron pairs in the outermost shell. The following electronic formulas represent several substances readily reacting to form complex ions:

$$H:\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle H}{\ddot{O}}}: \qquad H:\overset{\displaystyle\cdot\cdot}{\ddot{O}}: \qquad H:\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle H}{N}}:H \qquad :\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{S}}: \qquad :\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{Cl}}: \qquad :C:::N:$$

$$\quad\; H_2O \qquad\qquad OH^- \qquad\qquad NH_3 \qquad\qquad S^{--} \qquad Cl^- \qquad\qquad CN^-$$
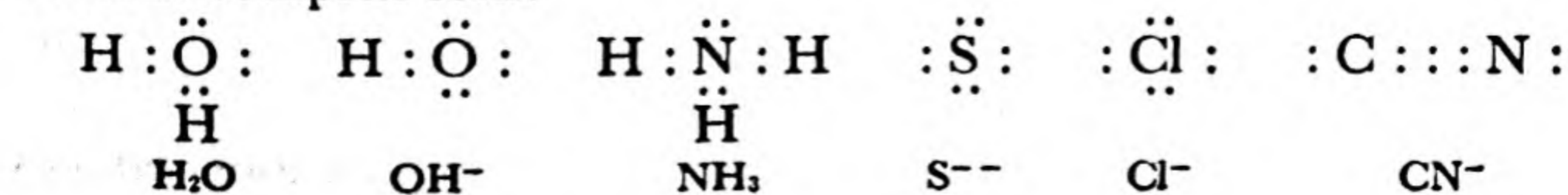
In each of the molecules and ions, the oxidation numbers are satisfied, but there are pairs of unshared electrons that may become shared in the formation of complex ions.

A number of metal ions form complex cations by adding neutral molecules and complex anions by adding negative ions. This property is especially prominent among the metals in the subgroups of the periodic system but is not limited to these elements. Many metal ions have electron arrangements that do not give completed structures. In a number of instances increased stability of structure is gained by sharing additional electron pairs with other ions or with molecules. It is assumed that these added electron pairs may enter an incomplete electron shell or may establish a new shell. The atomic number of copper is 29, but there are only twenty-seven electrons in the cupric ion. It is assumed that these electrons are distributed in three shells containing two, eight, and seventeen electrons, respectively. The cupric ion may add four molecules of ammonia to form the cupric ammonia complex ion, $Cu(NH_3)_4^{++}$, or four chloride ions to form the chlorocuprate ion, $CuCl_4^{--}$. Elec-
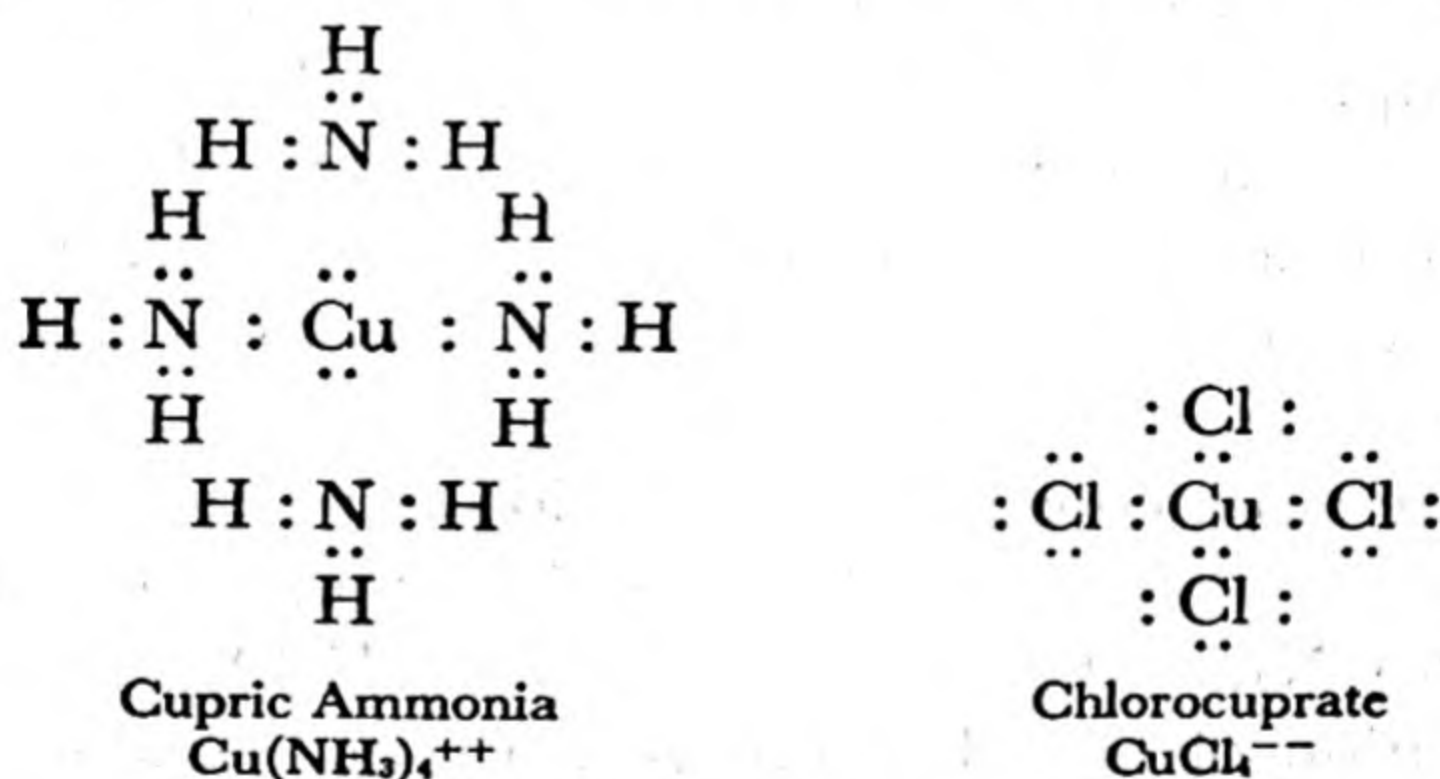
Fig. 88. Complex Ions

tronic formulas for these ions are shown in Fig. 88. The distribution of electrons about the nucleus of the copper ion in these complexes is 2, 8, 17, 8.

Stable complex ions are only slightly dissociated into the simpler products of which they are composed. Consequently, an ionization constant shows the relation between the concentrations of the simple constituents and the complex ion, as in other weakly dissociated electrolytes. The formation of stable complex ions reduces

the concentrations of the simple ions so greatly as to cause ionic reactions to proceed practically to completion. The formation of complex ions is often applied in dissolving slightly soluble substances and in setting up conditions that prevent precipitation. Such applications are illustrated in the following paragraph dealing with ammonia complex ions. Other complex ions are discussed in subsequent sections of the text.

Ammonia Complex Ions. A number of the metal ions yield complex cations with ammonia, e.g., $Ag(NH_3)_2{}^+$, $Cu(NH_3)_4{}^{++}$, $Zn(NH_3)_4{}^{++}$, $Ni(NH_3)_6{}^{++}$, and $Co(NH_3)_6{}^{++}$. These ions are fairly stable in solution in the presence of an excess of ammonia, but are decomposed by acids. The formation of these complex ions reduces the concentrations of the simple metal ions so greatly that the hydroxides of these metals do not precipitate from solutions containing an excess of ammonia. This principle may be applied in the separation of certain of the metal ions, e.g., the zinc and aluminum ions. When an excess of ammonia is added to a solution containing both of these ions, zinc ions yield ammonia complex ions but aluminum ions do not.

$$Zn^{++} + 4\,NH_3 \rightleftharpoons Zn(NH_3)_4{}^{++}$$
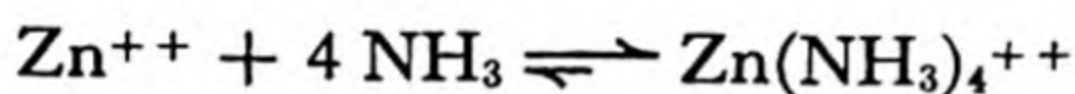
The complex ion is so stable in solutions containing an excess of ammonia that only low concentrations of free zinc ions may remain at equilibrium.

$$\frac{[Zn^{++}] \times [NH_3]^4}{[Zn(NH_3)_4{}^{++}]} = K$$

The zinc ion concentration is so small that the hydroxide does not precipitate.

$$[Zn^{++}] \times [OH^-]^2 < S_{Zn(OH)_2}$$

Aluminum hydroxide does precipitate from this solution.

$$[Al^{+++}] \times [OH^-]^3 > S_{Al(OH)_3} = 1.9 \times 10^{-33}$$
$$Al^{+++} + 3\,OH^- \rightleftharpoons Al(OH)_3 \downarrow$$

Silver chloride dissolves in a solution of ammonia because the formation of silver ammonia complex ions reduces the concentration of free silver ions to a lower value than required for equilibrium with the precipitate.

$$AgCl \downarrow \rightleftharpoons Ag^+ + Cl^-$$

$$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2{}^+$$

$$\frac{[Ag^+] \times [NH_3]^2}{[Ag(NH_3)_2{}^+]} = K$$

$$[Ag^+] \times [Cl^-] < S_{AgCl} = 1.1 \times 10^{-10}$$
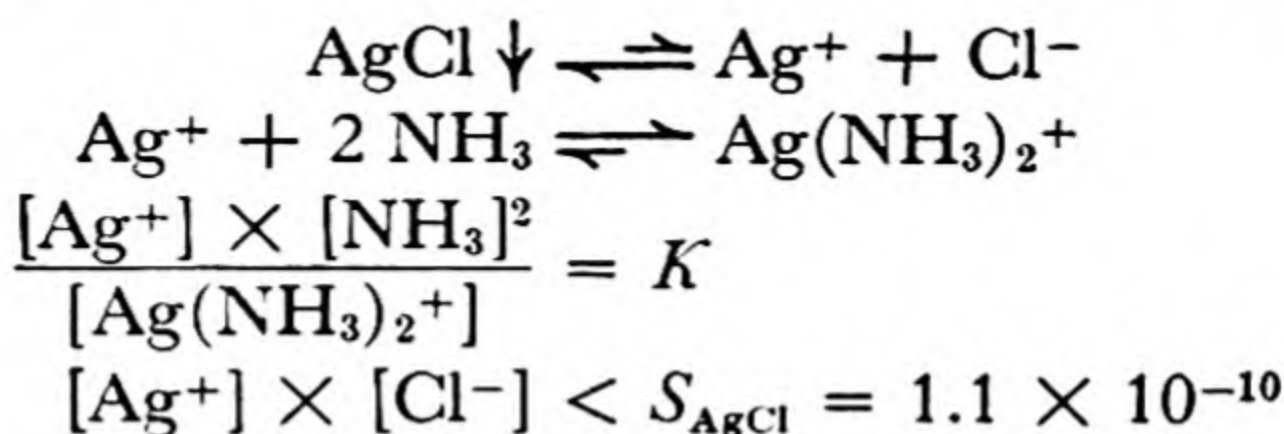
Consequently, silver chloride dissolves in an excess of ammonia.

$$AgCl \downarrow + 2\,NH_3 \longrightarrow Ag(NH_3)_2{}^+ + Cl^-$$
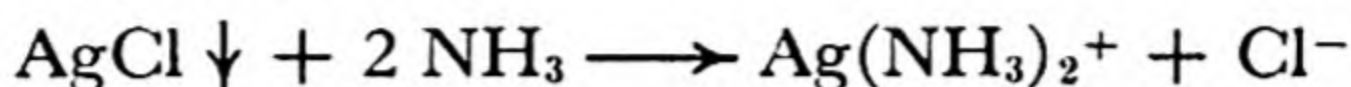
The solubility of silver iodide is too small to cause the formation of the complex ion in significant concentration.

$$\frac{[Ag^+] \times [NH_3]^2}{[Ag(NH_3)_2{}^+]} < K$$

Since the concentration of silver ions is not reduced, the equilibrium between silver iodide and its ions is not affected.

$$AgI \downarrow \rightleftharpoons Ag^+ + I^-$$

$$[Ag^+] \times [I^-] = S_{AgI} = 8.5 \times 10^{-17}$$
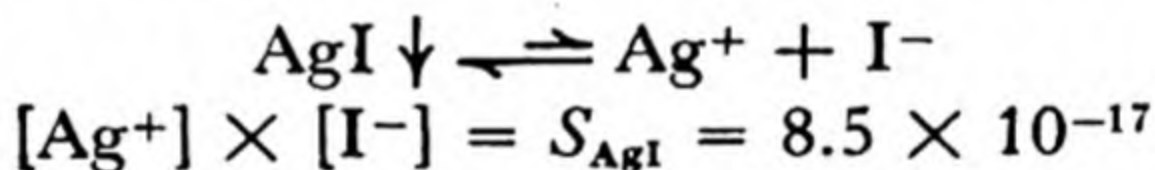
Therefore, silver iodide does not dissolve in solutions of ammonia. Silver bromide is intermediate in solubility to the chloride and iodide.

$$[Ag^+] \times [Br^-] = S_{AgBr} = 3.3 \times 10^{-13}$$

Silver bromide does not dissolve readily in dilute solutions of ammonia, but does dissolve in concentrated solutions.

EXERCISES

1. What is meant by a double decomposition reaction?
2. What general condition is required to cause the completion of double decomposition reactions involving ionic substances? List three types of reactions which produce this result, and illustrate each type by an equation.
3. What is meant by the solubility product of a substance? In terms of the solubility product principle, what condition is necessary to cause the formation of a precipitate?
4. For each of the classes of slightly soluble substances mentioned in the summary of solubilities, select an example. Indicate for each of the substances selected:
   (a) the solutions you would use to produce this substance as a precipitate;
   (b) the ionic equation for the reaction; (c) the solubility product expression;
   (d) the condition — in terms of solubility product — which leads to the formation of the precipitate.
5. What condition is required to cause a precipitate to dissolve? On the basis of general solubility relationships, suggest a reaction for dissolving the precipitates formed in Exercise 4.

6. Explain the fact that the formation of a weak electrolyte or of a gaseous substance causes an ionic reaction to proceed practically to completion.
7. What is meant by a complex ion? How is complex ion formation explained in terms of electronic structures?
8. Explain each of the following observations in terms of the solubility product principle and of the ionic equilibria employed to control ion concentrations.
   (a) Calcium carbonate dissolves in dilute hydrochloric acid solution
   (b) Barium sulfate does not dissolve in dilute hydrochloric acid solution
   (c) Calcium phosphate dissolves in nitric acid solution
   (d) Aluminum hydroxide is precipitated by adding an excess of ammonia solution to an aluminum salt
   (e) Zinc hydroxide is not precipitated by an excess of ammonia
   (f) Silver chloride dissolves in an excess of an aqueous solution of ammonia, but silver iodide does not

SUPPLEMENTARY READINGS

Hammett, L. D., *Solutions of Electrolytes*, McGraw-Hill Book Company, Inc., New York, 1936, chaps. II–III, V.

Hogness, T. R., and W. C. Johnson, *Qualitative Analysis and Chemical Equilibrium*, Henry Holt and Company, Inc., New York, 1937.

Creighton, H. J., and W. A. Koehler, *Electrochemistry*, John Wiley & Sons, Inc., New York, 1935, Vol. I, chap. XXIII.

Getman, F. H., and F. Daniels, *Outlines of Theoretical Chemistry*, John Wiley & Sons, Inc., New York, 1943, chap. XVII.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, American Book Company, New York, 1936, chap. X.

Chapter 17

ACIDS. BASES. AMPHOLYTES. HYDROLYSIS

According to the Arrhenius theory of ionization, acids are hydrogen compounds which dissociate in aqueous solution to yield hydrogen ions, while bases are the hydroxides of metals that yield hydroxide ions. Water itself is slightly ionized and, in terms of this theory, a neutral solution contains the same concentration of hydrogen and hydroxide ions as water. Acidic solutions contain a higher concentration of hydrogen ions than water, and basic solutions, a higher concentration of hydroxide ions. These definitions are satisfactory for many purposes. However, there are other substances, which in aqueous solution exhibit reactions of the same general nature as the acids and the basic hydroxides. There are also ions in solvents other than water, with reactions analogous to those of acids and bases in aqueous solution. A broader definition of acids and bases is based on their most important and characteristic reactions rather than on their composition or the specific ions present in their solutions.

Acids and Bases. According to the Lowry and Brönsted definitions, *acids are substances that may give up protons, the charged nuclei of hydrogen atoms, and bases are substances that may combine with protons.* Since the removal of a proton from an acid molecule is a reversible process, the anions of the acids have basic properties. The relation of the acid to the base in terms of the proton exchange is shown by the following equation:

$$\text{Acid} \rightleftharpoons \text{Proton} + \text{Base}$$
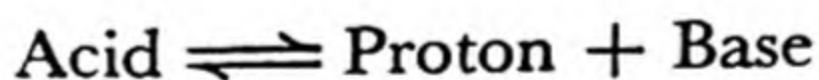
No measurable concentration of free protons is produced in a solution in equilibrium with the molecular acid, but, according to this theory, the change occurs in the presence of a proton acceptor. As discussed in Chapter 14, the ionization of an acid is assumed to involve a transfer of protons from acid molecules to water mole-

cules. Therefore, water is a base in this reaction. In its simplest form, the acid-base relationship is shown by the following equilibrium equation:

$$\text{Acid (1)} + \text{Base (2)} \rightleftharpoons \text{Acid (2)} + \text{Base (1)}$$
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
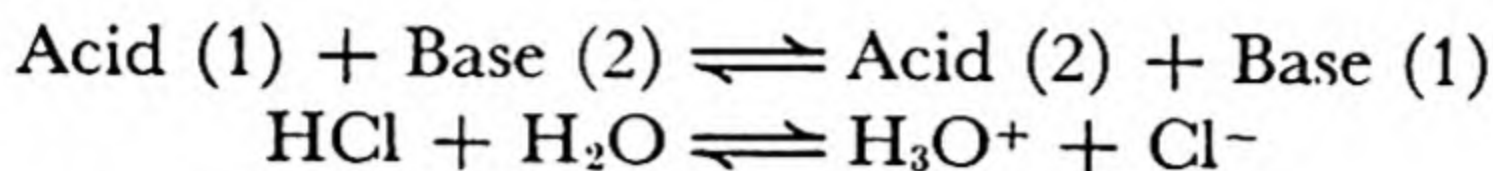
The transfer of a proton from one molecule or ion to another is *protolysis*. In this competition for the proton, the equilibrium concentrations depend on the relative strength of the acids and bases involved.

Acids. According to the proton-donor definition, the acids may be grouped into three classes, *viz.*, neutral acids, anion acids, and cation acids. *The neutral acids* are the familiar molecular acids that yield hydronium ions in aqueous solution. Strong acids readily split off protons and in dilute solutions exist almost entirely in the ionic state. Nitric acid is a strong acid.

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$
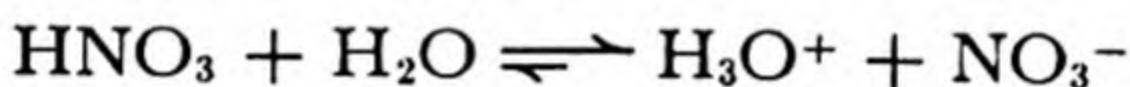
In weak acids the proton is held so firmly in the molecule that, even in dilute solutions, only a small percentage of the solute is in the ionic state at equilibrium.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$
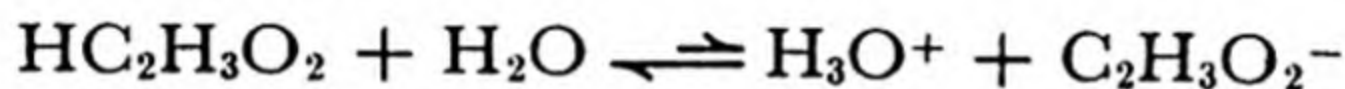
Water is a very weak acid, since the concentration of hydronium ions in pure water is low.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
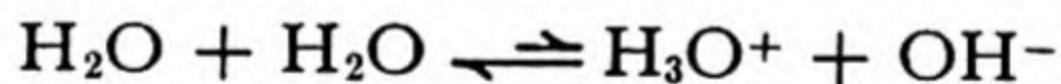
Only molecular substances that give up protons more readily than water exhibit acidic properties in aqueous solution.

The anion acids are anions that may give up protons, *i.e.*, anions containing replaceable hydrogen. These anions may be formed by the reaction of acid molecules containing two or more replaceable atoms of hydrogen. Neutral acid molecules of this type, such as sulfuric acid and phosphoric acid, ionize in more than one stage, and the primary stage is more extensive than the subsequent stages.

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$
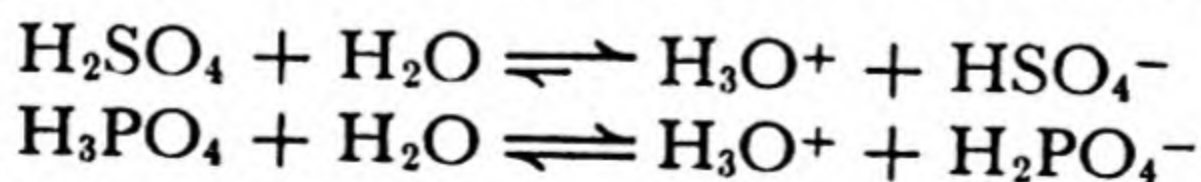
By reaction with a strong base such as sodium hydroxide, one proton from each molecule of the acid may be removed almost

completely before the removal of a second proton, thus producing anion acids from neutral acids.

$$H_2SO_4 + OH^- \longrightarrow H_2O + HSO_4^-$$
$$H_3PO_4 + OH^- \rightleftharpoons H_2O + H_2PO_4^-$$
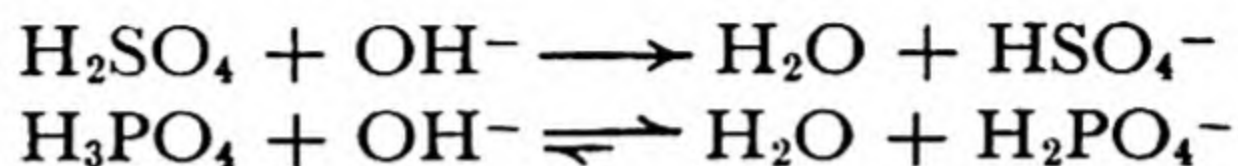
These anions, called hydrogen sulfate ion and dihydrogen phosphate ion, respectively, ionize to a smaller degree than the neutral acids from which they are formed.

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--}$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{--}$$
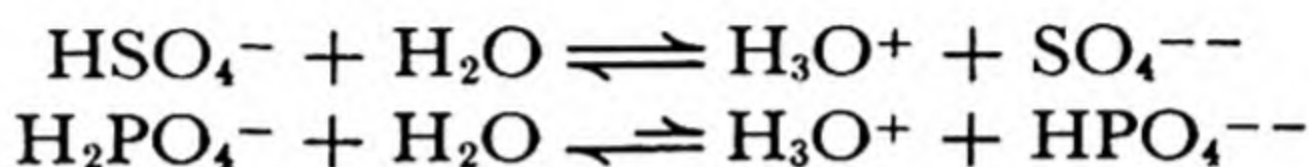
The monohydrogen phosphate ion is a very weak acid.

$$HPO_4^{--} + H_2O \rightleftharpoons H_3O^+ + PO_4^{---}$$
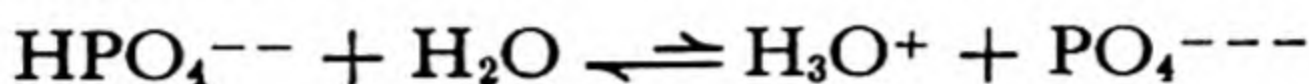
The cation acids are positive ions that may give up protons. The most important of these is the hydronium ion, which readily gives up protons to stronger bases such as the hydroxide ion.

$$H_3O^+ + OH^- \rightleftharpoons 2 H_2O$$
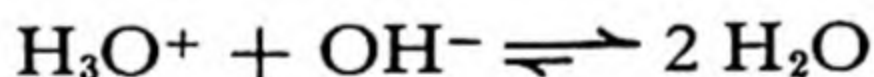
The ammonium ion, NH_4^+, also has acidic properties. The extent of its reaction with water is small, but is large with soluble hydroxides of metals.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$
$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$$
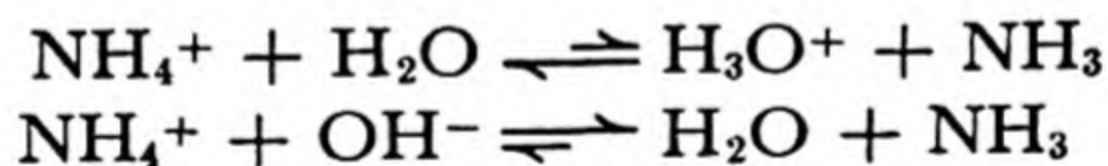
Many of the metal ions in solution become surrounded by water molecules to form hydrated ions. Some of these cations hold water molecules so loosely that no stable bond appears to be formed, and salts containing such ions crystallize from the solution without water of hydration. Other cations hold definite numbers of water molecules in combination, and hydrated salts, more or less stable toward heat, may be crystallized from solutions containing such ions. It is assumed that water molecules are held in combination with metal ions through the formation of coordinate bonds involving electron pairs in the oxygen atoms of the water molecules. It may be assumed further that in many of the hydrated ions the oxygen atom is attracted so strongly toward the kernel of the central atom of the cluster that the water molecules are distorted. In these distorted molecules, protons are repelled by the charge of the cation so that they can be split off to form hydronium ions more readily

than in free water molecules. Hydrated cations interacting with water molecules to form hydronium ions are cation acids. Hydrated cupric ions, $Cu(H_2O)_4^{++}$, and hydrated aluminum ions, $Al(H_2O)_6^{+++}$, are cation acids which give low concentrations of hydronium ions in aqueous solution.

$$Cu(H_2O)_4^{++} + H_2O \rightleftharpoons H_3O^+ + Cu(H_2O)_3(OH)^+$$
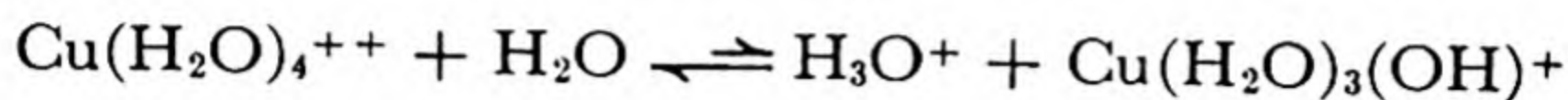
The coordination number of 4, characteristic of the cupric ion, does not change during this reaction.

Substances containing either anion acids or cation acids also contain enough ions of the opposite sign to balance the electric charges they bear. Thus, a solution of an anion acid contains cations, such as sodium or potassium ions, and a solution of a cation acid contains anions, such as chloride, nitrate, or sulfate. Although, strictly speaking, it is the ion that shows the acid properties, the salt, which contains the anion or cation acid, is commonly called an acidic substance, *e.g.*, sodium hydrogen sulfate, $NaHSO_4$, ammonium chloride, NH_4Cl, and hydrated aluminum chloride, $Al(H_2O)_6Cl_3$.

Bases. According to the proton-acceptor definitions, bases fall into two important groups, *viz.*, anion bases and neutral or molecular bases. *Anion bases* are the negative ions of molecular acids including water among these substances. The negative ions of the strong acids are weak bases, for they show little tendency to take up protons and form molecular acids in aqueous solution, but the negative ions of the weaker acids are stronger bases. These ions are introduced into solution along with equivalent concentrations of cations. Consequently, it is customary to extend the definition of the base to include the substances containing anion bases. The hydroxide ion is an active base, and sodium and potassium hydroxides are called bases.

The hydroxide ion is the strongest of the anion bases found in significant concentration in aqueous solution. Its reaction with hydronium ions yields water as a weakly ionized product.

$$H_3O^+ + OH^- \rightleftharpoons 2 H_2O$$
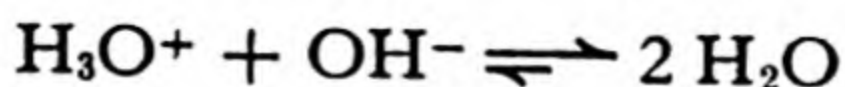
According to the law of molecular concentrations (see page 223) the ionization constant of water is:

$$\frac{[H_3O^+] \times [OH^-]}{[H_2O]^2} = K$$

The molar concentration of water in dilute solution is practically constant. Hence, the product of the molar concentrations of the ions of water is itself equal to a constant commonly called the ionization constant of water. At 20°, the concentration of each variety of ion furnished by water is equal to 1×10^{-7} molar, and the ionization constant of water is:

$$[H_3O^+] \times [OH^-] = K = 1 \times 10^{-14}$$

This ionization constant is smaller than the ionization constants of most of the weak acids. Even weak acids, such as hydrogen sulfide and the ammonium ion, react with solutions containing high concentrations of hydroxide ions.

$$H_2S + OH^- \rightleftharpoons H_2O + HS^-$$
$$HS^- + OH^- \rightleftharpoons H_2O + S^{--}$$
$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$$
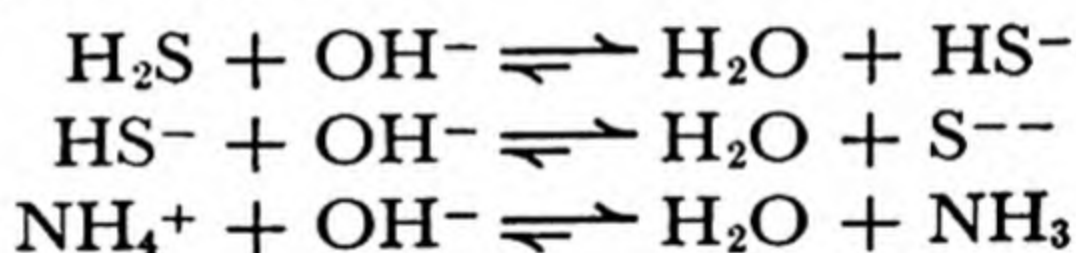
The metal hydroxides that are appreciably soluble in water furnish hydroxide ions and exhibit basic properties in solution. Formerly, metal hydroxides were the only substances classified as bases, but they are now considered to be one of a number of varieties of bases.

The acetate ion is the anion of a weak acid. Consequently, the addition of sodium acetate to a solution of a strong acid causes a decrease in the concentration of the hydronium ion, as shown by the ionization constant of acetic acid.

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K = 1.8 \times 10^{-5}$$

If 0.1 mole of sodium acetate is added to a liter of 0.1 molar hydrochloric acid solution, the ion concentrations at equilibrium are approximately equal to those in a 0.1 molar solution of acetic acid.

$$H_3O^+ + C_2H_3O_2^- \rightleftharpoons H_2O + HC_2H_3O_2$$
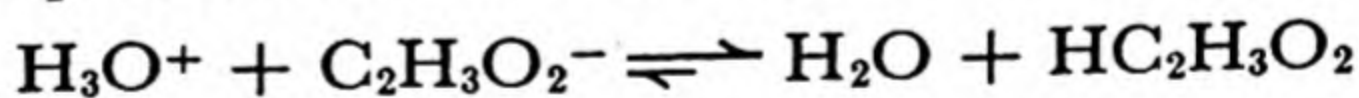
This causes a decrease in the hydronium concentration from approximately 0.1 to 0.00136 molar.

The carbonate and bicarbonate ions are anion bases, but the carbonate ion is more strongly basic. Carbonate ions take up protons to form bicarbonate ions.

$$H_3O^+ + CO_3^{--} \rightleftharpoons H_2O + HCO_3^-$$
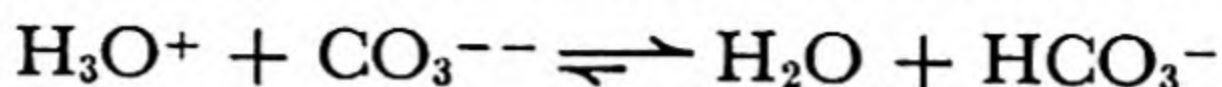
The dissociation constant for this ion is:

$$\frac{[H_3O^+] \times [CO_3^{--}]}{[HCO_3^-]} = K = 4.7 \times 10^{-11} \text{ at } 20°$$

The next stage of the reaction occurs in the presence of higher concentrations of hydronium ions, with the formation of water and carbon dioxide.

$$H_3O^+ + HCO_3^- \rightleftharpoons 2 H_2O + CO_2$$
$$\frac{[H_3O^+] \times [HCO_3^-]}{[CO_2]} = K = 4.3 \times 10^{-7}$$
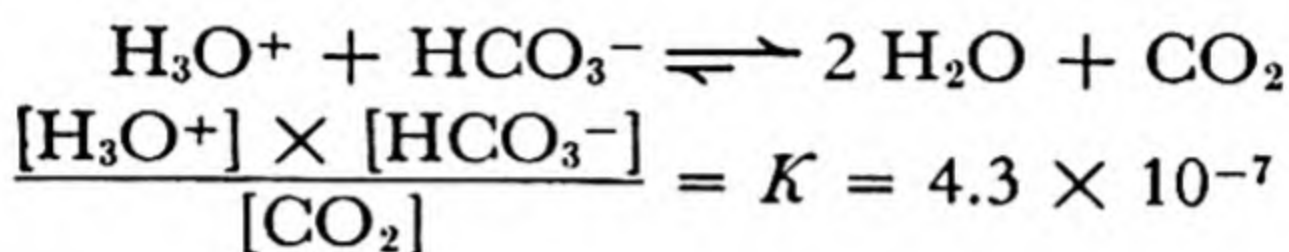
Sulfide, cyanide, borate, silicate, and phosphate ions are other anion bases. The concentration of hydronium ions in a solution of an anion base depends on the equilibrium concentrations expressed by the ionization constant of the weak acid formed in the reaction.

Molecular bases are molecular substances that may take up protons to form cation acids. Ammonia and water are common molecular bases. Ammonia reacts to some extent with water, but to a greater extent with acids stronger than water.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$
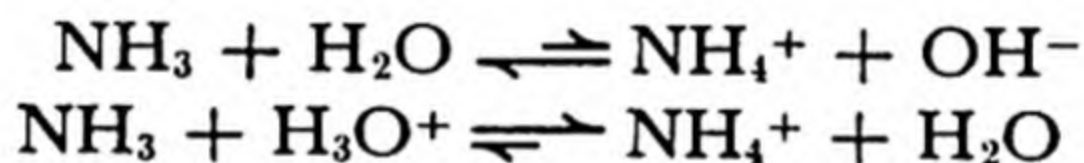
According to present definitions, the combination of water with protons is the fundamental reaction of the ionization of molecular acids. The oxides of some of the metals have a molecular structure in the solid state, and these oxides react with hydronium ions in acidic solutions to form water and free ions of the metal. The oxides of some of the active metals have an ionic structure. The basic properties of such oxides may be attributed in part to combination with water forming hydroxide ions, and in part to the direct reaction of oxide ions at the surface of the solid with hydronium ions in solution.

$$CaO + H_2O \longrightarrow Ca^{++} + 2 OH^-$$
$$CaO + 2 H_3O^+ \longrightarrow Ca^{++} + 3 H_2O$$
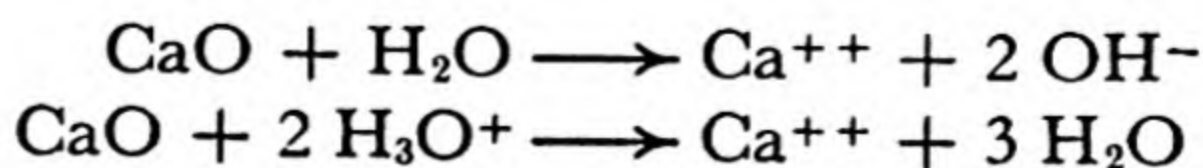
Corresponding Acids and Bases. It has been shown in preceding paragraphs, that, in general, the reactions of acids and bases

with each other are reversible. Acids and bases that bear the relation indicated by the equation

$$\text{Acid} \rightleftharpoons \text{Base} + \text{Proton}$$

are called *corresponding or conjugate acids and bases*. In Table 25 a number of corresponding acids and bases are listed. A more extensive list may be found in Appendix, Table XI.

TABLE 25. CORRESPONDING ACIDS AND BASES

ACID		BASE	
Name	*Formula*	*Name*	*Formula*
Hydrochloric acid	HCl	Chloride ion	Cl^-
Hydronium ion	H_3O^+	Water	H_2O
Hydrosulfate ion	HSO_4^-	Sulfate ion	SO_4^{--}
Acetic acid	$HC_2H_3O_2$	Acetate ion	$C_2H_3O_2^-$
Ammonium ion	NH_4^+	Ammonia	NH_3
Zinc hydroxide	$Zn(OH)_2$	Zincate ion	$Zn(OH)_4^{--}$
Hydrated cupric ion	$Cu(H_2O)_4^{++}$	Cupric hydroxy ion	$Cu(H_2O)_3(OH)^+$
Water	H_2O	Hydroxide ion	OH^-
Hydroxide ion	OH^-	Oxide ion	O^{--}

Since hydrochloric acid is a strong acid in aqueous solution, the basic properties of chloride ions in dilute solutions are insignificantly small. Nevertheless, chloride ions readily take up protons in the reaction of concentrated sulfuric acid with solid sodium chloride, because hydrogen chloride is not ionic under these conditions. Hydronium ions are less active in releasing protons than hydrogen chloride molecules, and water is more actively basic than the chloride ion. The ammonium ion is a much weaker acid than hydrochloric acid, and, as a consequence, the corresponding base, ammonia, is an active base. The hydroxide ion may suffer the loss of a proton under some conditions, thus exhibiting the reaction of an acid, but this reaction does not occur in aqueous solution, because the oxide ion is too strongly basic to exist in other than very low concentrations in solution.

Ampholytes. There are a number of substances which are both acids and bases, *i.e.*, they may give up protons and they may also combine with protons. These substances are known as *ampholytes* or *amphoteric electrolytes*. Examples of substances showing these properties have been encountered previously. The ionization of water involves the transfer of protons between water molecules.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
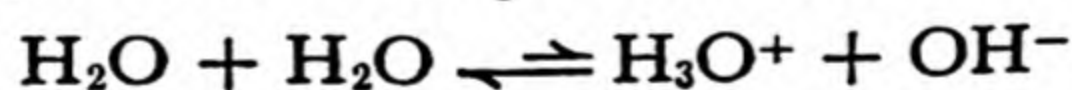
The bicarbonate ion is both an acid and a base.

$$HCO_3^- + H_3O^+ \rightleftharpoons 2\,H_2O + CO_2$$
$$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{--}$$
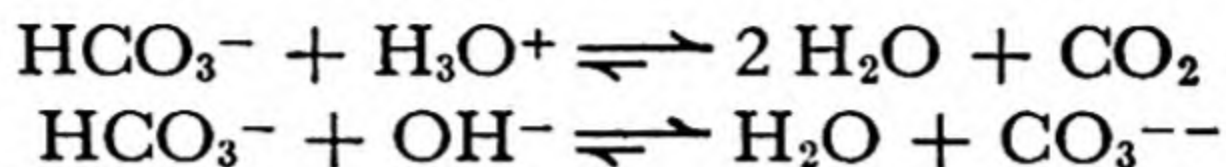
A number of hydroxides and hydroxide complex products are ampholytes.

Amphoteric Hydroxides. The acid-base properties of the hydroxides of the metals vary greatly. The hydroxides of the elements in the third period of the periodic system illustrate this relationship. Sodium hydroxide is strongly basic, while magnesium hydroxide is less actively basic than sodium hydroxide, and aluminum hydroxide is amphoteric. The hydroxides of silicon, sulfur, phosphorus, and chlorine are acidic. The hydroxide of chlorine in its low positive oxidation state is weakly acidic.

$$ClOH + H_2O \rightleftharpoons H_3O^+ + ClO^-$$
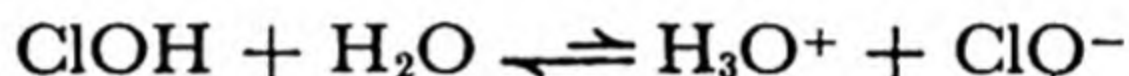
This compound is commonly called hypochlorous acid and is represented by the formula $HClO$. The acidity of the hydroxide of an element increases with the oxidation number, and perchloric acid, $HClO_4$, the hydroxy compound of chlorine in its highest oxidation state, ClO_3OH, is a strong acid.

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$$
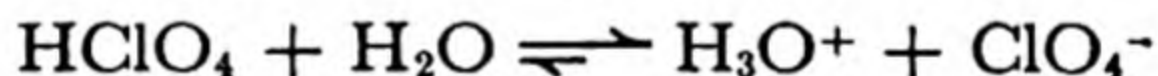
As the atomic numbers of the elements in a period in the periodic system become progressively one unit larger, the basic nature of the hydroxide decreases and the acidic nature increases. As the oxidation number of a specific nonmetal increases, the acidity of its hydroxide becomes greater.

A consideration of the following points may explain these relationships in terms of the theories of atomic structure. The acidic or basic nature of the hydroxide of an element depends on the relative force of attraction between oxygen and hydrogen in the hydroxide group, and the force between oxygen and the kernel of the atom to which the hydroxide group is joined. The force with which oxygen is bound increases as the positive charge of the kernel of the atom increases and the size decreases. In a period of elements, such as those mentioned in the preceding paragraph, the kernels of the atoms have similar electronic structures, but the charge of the nucleus increases by successive units as the atomic numbers become

greater. Similarly, the radii of the kernels of these atoms decrease as the atomic numbers increase. Just as the oxygen atom, the negative part of the hydroxide group, is held more firmly as the distance between the atoms decreases and the charge increases, so the proton is repelled and is held less firmly. Similarly, as the oxidation number of an individual atom is made larger, the unbalanced charge of the kernel of the atom is assumed to increase, and the bond between hydrogen and oxygen to become weaker. Consequently, the proton is more readily detached by a proton acceptor, and the acid strength is increased.

Reactions of Amphoteric Hydroxides. A consideration of the preceding paragraphs suggests that the hydroxides of many of the elements are amphoteric. The hydroxides of aluminum, zinc, stannous tin, lead, chromium, and antimony are common amphoteric hydroxides. The cations in these compounds are hydrated complex ions which tend to retain a constant coordination number. Consequently, the hydroxides of these metals contain enough hydroxide groups to satisfy the oxidation numbers, and enough additional molecules of water to make the total number of groups associated with the ion equal to the coordination number. Aluminum hydroxide may be represented by the formula, $Al(H_2O)_3(OH)_3$, and zinc hydroxide by the formula, $Zn(H_2O)_2(OH)_2$. The amphoteric hydroxides in general have low solubility and are so weakly basic that they produce no significant concentration of either hydronium or hydroxide ions. Nevertheless, the amphoteric hydroxide may give up protons to stronger bases and may take on protons from stronger acids. Aluminum hydroxide, for example, reacts with sodium hydroxide with the formation of water and of the complex aluminum hydroxide ion, known as the aluminate ion. In this reaction aluminum hydroxide is an acid.

$$Al(H_2O)_3(OH)_3 \downarrow + OH^- \rightleftharpoons H_2O + Al(H_2O)_2(OH)_4^-$$
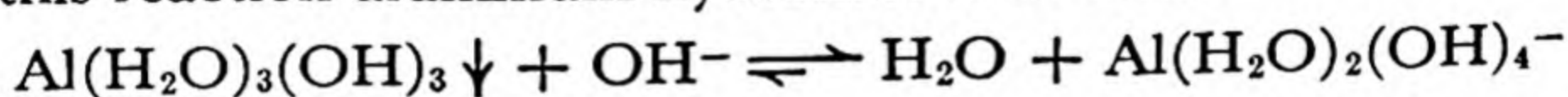
The complex ion may react further as an acid anion with an excess of sodium hydroxide.

$$Al(H_2O)_2(OH)_4^- + OH^- \rightleftharpoons H_2O + Al(H_2O)(OH)_5^{--}$$
$$Al(H_2O)(OH)_5^{--} + OH^- \rightleftharpoons H_2O + Al(OH)_6^{---}$$
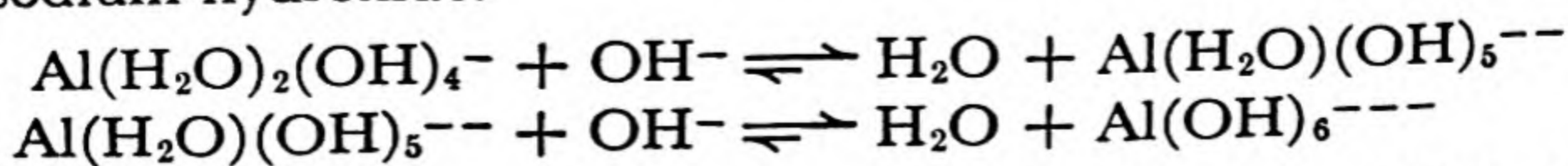
Aluminum hydroxide also reacts as a molecular base. With strong acids it may form a series of complex cations, yielding finally the

hydrated aluminum ion when an excess of acid is present in the solution.

$$Al(H_2O)_3(OH)_3 \downarrow + H_3O^+ \rightleftharpoons H_2O + Al(H_2O)_4(OH)_2{}^+$$
$$Al(H_2O)_4(OH)_2{}^+ + H_3O^+ \rightleftharpoons H_2O + Al(H_2O)_5(OH)^{++}$$
$$Al(H_2O)_5(OH)^{++} + H_3O^+ \rightleftharpoons H_2O + Al(H_2O)_6{}^{+++}$$
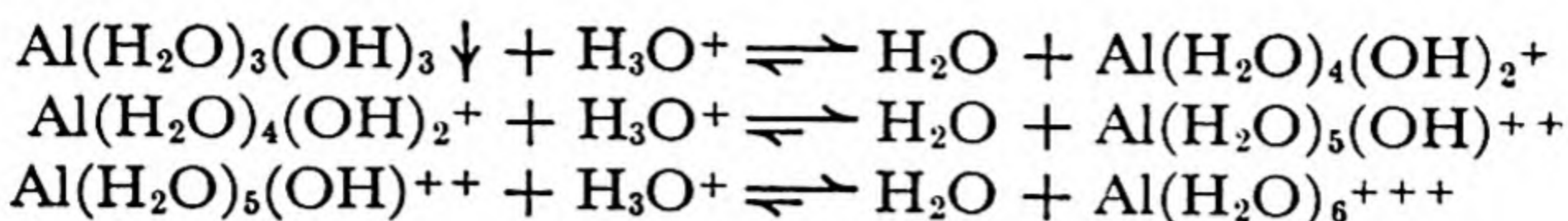
Preparation of Amphoteric Hydroxides. Since these substances are weakly ionized and slightly soluble, they may be prepared by precipitation methods. They separate from the solution, carrying an excess of water held loosely in the solid. Such precipitates are called *gelatinous precipitates.* They frequently have indefinite proportions of water, so that they are more properly called *hydrous oxides.* Zinc hydroxide may be precipitated by the reaction of sodium hydroxide with zinc sulfate. Zinc ions in solution are hydrated cations. The number of water molecules associated with each ion may be assumed to be four.

$$Zn(H_2O)_4{}^{++} + 2\,OH^- \rightleftharpoons 2\,H_2O + Zn(H_2O)_2(OH)_2 \downarrow$$
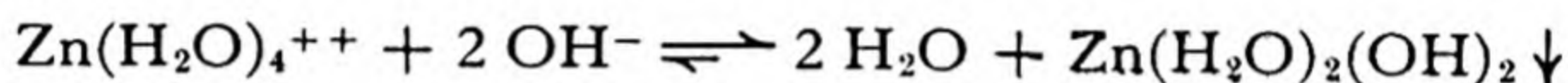
The precipitated hydroxide is acidic and reacts with an excess of hydroxide ions.

$$Zn(H_2O)_2(OH)_2 + 2\,OH^- \rightleftharpoons 2\,H_2O + Zn(OH)_4{}^{--}$$
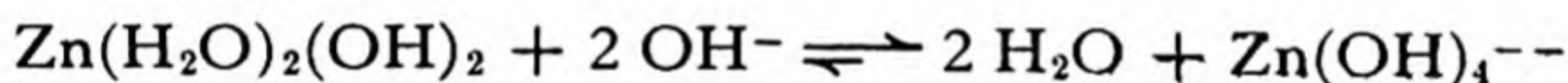
Consequently, either a weak base or limited proportions of a strong base must be used for the precipitation of the amphoteric hydroxides from solutions containing the cations of the metals. Zinc hydroxide may be precipitated also by the reaction of an acid with a solution containing the zincate complex ion, $Zn(OH)_4{}^{--}$.

$$Zn(OH)_4{}^{--} + 2\,H_3O^+ \rightleftharpoons 2\,H_2O + Zn(H_2O)_2(OH)_2 \downarrow$$
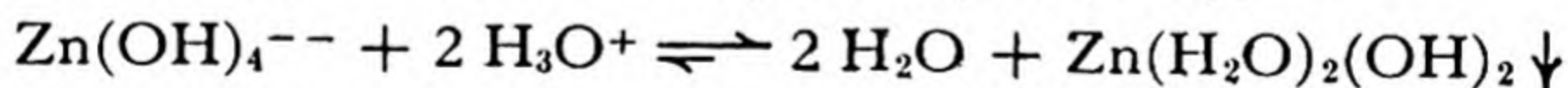
An excess of acid dissolves the precipitate to form a soluble zinc salt.

Aluminum hydroxide may be precipitated by the reaction of a limited quantity of sodium hydroxide with an aluminum salt, $Al(H_2O)_6{}^{+++}$, or by the reaction of a limited quantity of hydrochloric acid with an aluminate, $Al(H_2O)_2(OH)_4{}^-$ or $Al(OH)_6{}^{---}$.

$$Al(H_2O)_6{}^{+++} + 3\,OH^- \rightleftharpoons 3\,H_2O + Al(H_2O)_3(OH)_3 \downarrow$$
$$Al(OH)_6{}^{---} + 3\,H_3O^+ \rightleftharpoons 3\,H_2O + Al(H_2O)_3(OH)_3 \downarrow$$
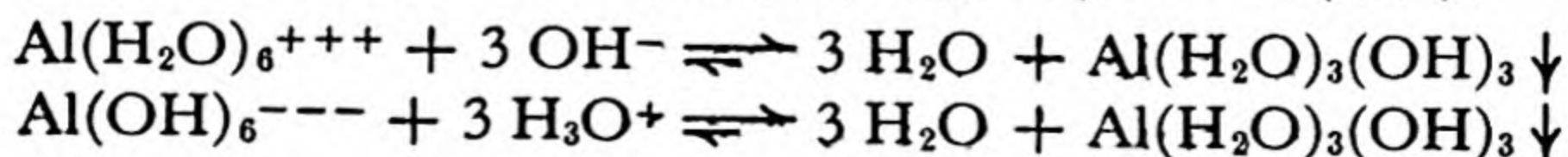
For many purposes the inclusion of waters of hydration in the formulas used in writing equations is unnecessarily cumbersome.

A simplification may be introduced by writing the formulas without waters of hydration. In simplified form, the precipitation of the hydroxides of zinc and aluminum may be represented by the following equations:

$$Zn^{++} + 2\ OH^- \rightleftharpoons Zn(OH)_2 \downarrow$$
$$Al^{+++} + 3\ OH^- \rightleftharpoons Al(OH)_3 \downarrow$$
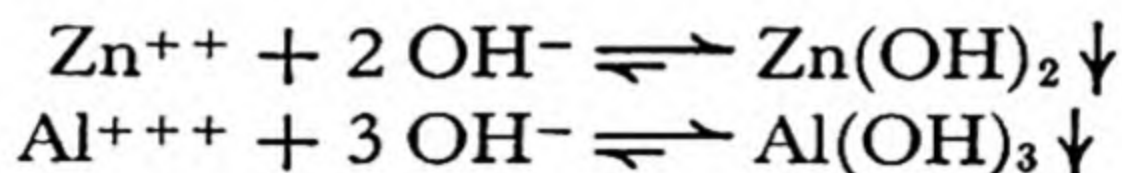
The equations for the reactions of these hydroxides with an excess of hydroxide ions may also be simplified.

$$Zn(OH)_2 \downarrow + 2\ OH^- \rightleftharpoons Zn(OH)_4^{--}$$
$$Al(OH)_3 \downarrow + OH^- \rightleftharpoons Al(OH)_4^-$$
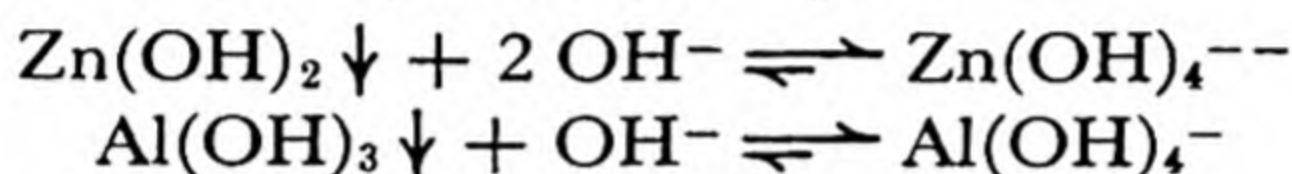
The simplified equations satisfactorily represent the precipitation of the hydroxides and their solution in an excess of sodium hydroxide. They are quite inadequate for showing the amphoteric nature of the hydroxide. The simplified equation does not show, for example, the liberation of protons in the formation of the zincate ions from zinc hydroxide, nor does it show the combination of the zincate ions with protons in the reverse process. Although the simplified equations are used extensively, and the precipitated hydroxides are commonly represented without water of hydration, the complete equation is necessary for an understanding of the acid-base relationships of the amphoteric hydroxides.

Neutralization. The concentrations of hydronium and hydroxide ions in solution are related to each other as shown by the equilibria in pure water. Omitting water of hydration the ionic equation is,

$$H^+ + OH^- \rightleftharpoons H_2O$$
$$[H^+] \times [OH^-] = 1 \times 10^{-14} \text{ at } 20°$$
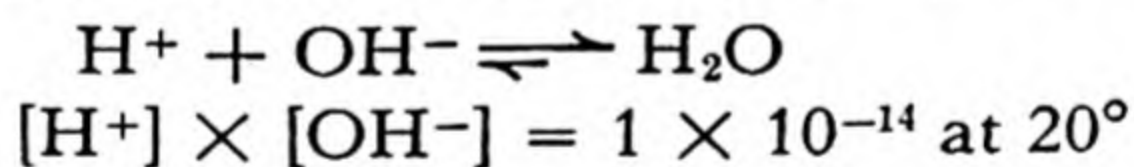
Solutions containing one of these ions in higher concentration than water must contain correspondingly lower concentrations of the other ion.

$$[OH^-] = \frac{K}{[H^+]} \qquad\qquad [H^+] = \frac{K}{[OH^-]}$$

In common practice, a solution containing equal concentrations of hydrogen and hydroxide ions is called a *neutral solution*. The definition is arbitrary, and some other concentration of these ions could have been selected as the point of neutrality. Since water is the common solvent in which many reactions occur, it is convenient to define neutrality in terms of its properties. Aqueous solu-

tions containing a greater concentration of hydrogen than hydroxide ions are acidic, and those containing smaller concentrations are basic. Chemical reactions that change the concentration of hydrogen ions to become the same as in pure water are called neutralization reactions. Strong acids may be neutralized by reaction with equivalent proportions of highly ionized basic hydroxides, and basic solutions may be neutralized by reaction with strong acids. Unless cations of the base and anions of the acid also unite, the same reaction occurs in the neutralization of any strong acid by any strong basic hydroxide, provided they are in dilute solution. This conclusion is confirmed by the fact that nearly the same amount of heat is evolved in the neutralization of equivalent quantities of any strong acid by any strong basic hydroxide in dilute solution. The number of calories of heat given out during the neutralization of one gram ion of hydrogen ions by reaction with hydroxide ions is called the *heat of neutralization*. The average value is 13,800 calories.

$$H^+ + OH^- \rightleftharpoons H_2O + 13,800 \text{ cal.}$$
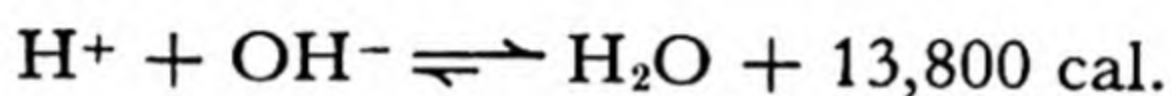
The heat evolved in this reaction is not always exactly the same because the activities of the ions are not the same in all acidic and basic solutions. The heat evolved during the neutralization of a weak acid is much less than this average value for strong acids.

The Significance of pH. The molar concentrations of both the hydrogen and hydroxide ions in aqueous solution are expressed by stating the concentration of either one. If the effective concentration, or activity, of the hydrogen ion in an aqueous solution is 1 M., the effective concentration of the hydroxide ion is 1×10^{-14} M. The unit for concentrations is so small that a range providing 1×10^{-14} divisions is required to express changes in concentration from a solution that is one molar with respect to hydrogen ions to one that is one molar with respect to hydroxide ions.

For many purposes a more compact scale is desired, and therefore it is more convenient to use the logarithm of the reciprocal of the hydrogen ion concentration, as proposed by Sörensen in 1909. This is designated pH.

$$p\text{H} = \log \frac{1}{[H^+]} = - \log [H^+].$$

The range from 1 to 1×10^{-14} on the scale of the hydrogen ion concentrations is expressed by numbers from 0 to 14 on this scale. In a solution in which the concentration of the hydrogen ion is 1 M., the pH is equal to 0. With decreasing concentration of the hydrogen ion, the pH increases one unit for each tenfold decrease in the hydrogen ion concentration. The concentration of the hydrogen ion is 1×10^{-7} in pure water, and the pH is 7. In a basic solution, in which the concentration of the hydrogen ion is 1×10^{-14}, the pH is 14. For unit changes in the negative exponent of the hydrogen ion concentration, the pH may be determined by inspection. For intermediate values it is necessary to use a table of logarithms. It is important to remember that the logarithm, as commonly written, consists of the sum of a characteristic, which may be either positive or negative, and a mantissa, which is always positive. The pH is a number in which both parts have the same sign. The following examples will illustrate the calculation of pH from the concentration of the hydrogen ion and of the concentration of the hydrogen ion from the pH. Suppose that the molar concentration of the hydrogen ion in a solution is 5.2×10^{-6}.

$$p\text{H} = \log \frac{1}{[\text{H}^+]} = -\log [\text{H}^+] = -(\bar{6}.72) = 5.28.$$

Suppose that the pH in a second solution is 3.64.

$$p\text{H} = 3.64 = \log \frac{1}{[\text{H}^+]}$$
$$\log [\text{H}^+] = -3.64 = \bar{4}.36$$
$$[\text{H}^+] = 2.3 \times 10^{-4}.$$

Indicators. An indicator is a conjugate acid-base system in which the acid and base differ in color. The acid is formed by reaction with hydrogen ions and the base by removal of hydrogen ions. The concentration of hydrogen ions at which these changes occur is characteristic of the substance used as the indicator. The changes are not abrupt and, consequently, the two forms of the indicator may exist together over a certain range of pH values. Indicators may be chosen which give a sharp color change within a particular pH range, and the acidity of many solutions may be determined directly by observing the color effects produced with

different indicators. Several indicators are listed in Table 26, together with the pH range and the characteristic colors.

TABLE 26. INDICATORS

| Indicator | pH Range | COLOR | |
		Acid	Base
Thymol blue	1.2–2.8	red	yellow
Brom phenol blue	3.0–4.6	yellow	blue
Methyl orange	3.1–4.4	red	yellow
Methyl red	4.2–6.3	red	yellow
Brom thymol blue	6.0–7.6	yellow	blue
Neutral red	6.8–8.0	red	yellow
Litmus	4.5–8.3	red	blue
Thymol blue (base)	8.0–9.6	yellow	red
Phenolphthalein	8.3–10.0	colorless	red

Indicators are also used for the determination of the end point in the reaction of an acid with a base. *The end point* is the point in the procedure which marks the reaction of equivalent quantities of acid and base. The solution may, or may not be neutral as defined by the properties of water, at the end point in the reaction of a particular acid with a base. The concentration of hydrogen ions, or pH, of the solution at the end point depends on the nature and concentration of the ions of the salt remaining in solution. A solution of sodium chloride is neutral, but a solution of ammonium chloride is acidic, while a solution of sodium acetate is basic. Hence, the indicator should be selected that shows the color change characteristic of the concentration of hydrogen ions in a solution of the salt produced during the reaction of the acid with the base.

Titration of Acids with Bases. The experimental determination of the concentration or quantity of an acid in a solution is known as *acidimetry* and of a base, as *alkalimetry*. This is accomplished by measuring accurately the volume of a solution of known concentration, a standard solution, required to react with a definite volume of an acidic or basic solution of unknown concentration. The procedure is called *titration*. The solutions may be placed in burettes from which the volumes required for the reaction are measured into the beaker below. An indicator should be chosen that shows a color change at the pH resulting from the reaction of equivalent quantities of the acid and base.

If the concentration of one of the solutions is known, the concentration of the other is easily calculated from the equivalent volumes. Suppose that it is found by experiment that 25.5 ml. of a 0.1 N. solution of a base neutralize 25.0 ml. of an acidic solution with a concentration to be determined. The acidic solution is the more concentrated one, and the normalities of the two solutions vary inversely with the volumes required for the reaction. Using the subscripts, A and B, to represent the acid and base, respectively, and N to represent the normality and V the volume:

$$\frac{N_A}{N_B} = \frac{V_B}{V_A}$$

or,

$$N_A V_A = N_B V_B$$

$$N_A = \frac{25.5 \times 0.1}{25.0} = 0.102$$

Suppose that it is desired further to calculate the dilution of the acid that would be required to make it 0.1 N. Since the volumes vary inversely with the normalities, the product of the normality multiplied by the volume is constant.

$$N_1 V_1 = N_2 V_2$$
$$0.102 \ V_1 = 1000 \times 0.1$$
$$V_1 = 980.4 \text{ ml.}$$

That is, 980.4 ml. of this acid are required for each liter of exactly 0.1 N. solution.

The weight of an acid or base in a solution may be determined by measuring the volume of a standard solution equivalent to it. Suppose that 31.56 ml. of 0.2 M. hydrochloric acid solution are required to neutralize the sodium hydroxide in an unknown solution.

$$H^+ + OH^- \rightleftharpoons H_2O$$
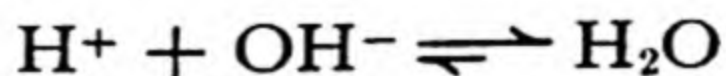
One mole of hydrochloric acid reacts with one mole, 40 g., of sodium hydroxide. Since the hydrochloric acid solution is 0.2 M., one liter contains 0.2 mole of hydrochloric acid. The volume of the solution required for reaction, 31.56 ml., is equal to 31.56×0.001 liter. Hence, the weight of the sodium hydroxide in the unknown solution is:

$$40 \times 0.2 \times 0.03156 = 0.252 \text{ g. of sodium hydroxide}$$

Buffer Solutions. The addition of a salt of a weak acid to a solution of the acid decreases the concentration of the hydrogen ion. The addition of a salt of a weak base to a solution of the base decreases the concentration of the hydroxide ion. This effect is most readily understood by consideration of the acid-base equilibria. When sodium acetate is added to a solution of acetic acid, the concentration of the anion base is increased. Therefore, the equilibrium between this ion and the hydrogen ion is disturbed, so that a lower concentration of the hydrogen ion remains in solution than would in the absence of the salt.

$$H^+ + C_2H_3O_2{}^- \rightleftharpoons HC_2H_3O_2$$
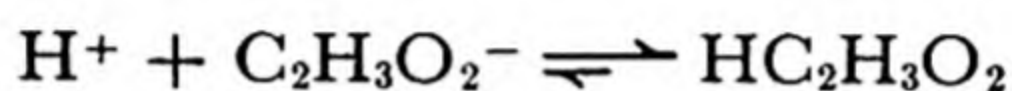
If small additional quantities of hydrogen ions are introduced into this solution, a further reaction with acetate ions takes place, and the concentration of hydrogen ions remains practically constant. If hydrogen ions are removed from the solution by reaction with some stronger base, the molecular acetic acid serves as a reservoir to keep the concentration at practically its former value. Consequently, such solutions resist changes in the concentration of the hydrogen ion. Solutions containing a regulated low concentration of the hydrogen ion, together with molecular substances and ions which prevent significant changes in the concentration of the hydrogen ion, are known as *buffer solutions*. By varying the concentrations of the acid and salt and by selecting different weak acids and their salts, it is possible to prepare solutions buffered at different pH values.

Buffer solutions are important in analytical work when it is necessary to maintain a regulated concentration of hydrogen ions in order to secure the desired separation. Various animal fluids are highly buffered. The pH of the blood is controlled by a number of buffering substances. The presence of bicarbonates is especially important, because they may react with large additional quantities of acids without permitting any significant change in the pH.

The Hydrolysis of Ions. Ions furnished by many of the salts in aqueous solution react with water. Anions with active basic properties gain protons from water molecules, and cations, actively acidic, release protons with the formation of hydronium ions. Each of these reactions is reversible, and each leads to a state of

equilibrium, unless insoluble or inactive molecular products are formed. The reactions of the ions of a salt with water may take place independently of each other. Whether the solution of the salt is acidic, neutral, or basic depends on the relative acidity or basicity of the ions. The reaction involves the transfer of protons, a reaction of protolysis. A reaction in which water is an active agent in the proton transfer is called *hydrolysis*.

A number of reactions of this variety have already been discussed in preceding paragraphs. The ionization of acids to form hydronium ions, and of some bases to produce hydroxide ions, are reactions of hydrolysis. A consideration of the hydrolysis of ions is important in the study of the reactions of salt solutions. In addition to the ions of the salt, such solutions may contain significant concentrations of either hydronium or hydroxide ions. Solutions of salts composed of the cations of strong bases and of the anions of strong acids are neutral, because neither variety of ion is hydrolyzed to a significant degree.

Hydrolysis of Anion Bases. Anion bases are anions which take up protons to form acid molecules. Only those that form weakly ionized molecules react with water to a significant extent. When potassium cyanide dissolves in water it becomes dispersed into ions:

$$KCN \longrightarrow K^+ + CN^-$$
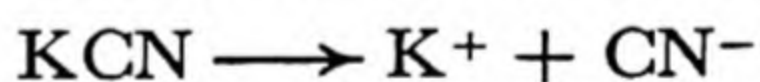
Hydrocyanic acid is a weak acid, and the cyanide ion reacts with hydronium ions from water to form the molecular acid.

$$H_3O^+ + CN^- \rightleftharpoons HCN + H_2O$$
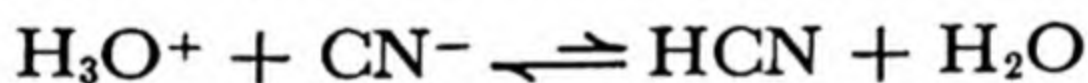
This reaction causes a decrease in the concentration of hydronium ions, and disturbs the equilibrium of water with its ions.

$$H_3O^+ + OH^- \rightleftharpoons 2 H_2O$$
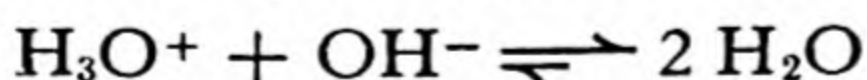
Consequently, additional water molecules dissociate to restore the water equilibrium. The changes continue until the concentrations of hydronium and cyanide ions have decreased, and the concentration of hydroxide ions has increased to such an extent that both equilibria may exist simultaneously in the same solution. Combining these two effects, the hydrolysis of the cyanide ion is shown by the equilibrium equation:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$
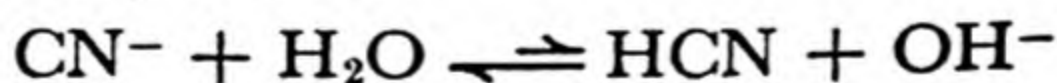
The reaction may be pictured as a competition between cyanide and hydroxide ions for protons. Since the degree of ionization of hydrocyanic acid is greater than that of water, equilibrium is established when only a small per cent of the cyanide has been converted into the molecular acid. In a 0.1 molar solution of potassium cyanide at 20°, the degree of hydrolysis is 1.2 per cent, and the concentration of the hydroxide ions is 1.2×10^{-3} molar.

The hydrolysis of soluble carbonates also produces basic solutions. The carbonate ion is an anion base that may combine with a proton to form the bicarbonate ion.

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-$$
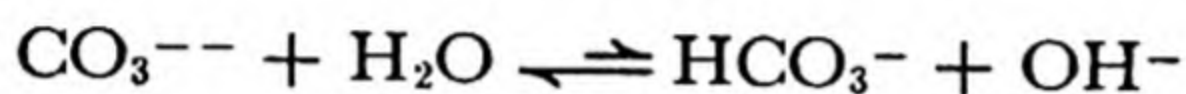
In this reaction, the competition for the proton is between carbonate and hydroxide ions. Since the carbonate ion is more strongly basic than the cyanide ion, the degree of hydrolysis of carbonates is greater than of cyanides. In a 0.1 molar solution of sodium carbonate at 20°, the degree of hydrolysis is 4 per cent, and the concentration of the hydroxide ion is 4×10^{-3}. In the presence of the products of the primary reaction, the secondary stage of a reaction of hydrolysis does not usually occur to an appreciable extent. The concentration of hydronium ions in the carbonate solution, satisfying the conditions for the carbonate-bicarbonate equilibrium, is not great enough to convert the bicarbonate into water and carbon dioxide.

The sodium and potassium salts of other weak acids, such as acetic, boric, silicic, and phosphoric acids, hydrogen sulfide and the amphoteric hydroxides, are similarly hydrolyzed to form basic solutions.

Hydrolysis of Cation Acids. Cation acids are positively charged ions that may give up protons. They undergo hydrolysis if they are active enough to release protons to the water molecules. The increased concentration of hydronium ions caused by this reaction requires a decreased concentration of hydroxide ions, and the solution is acidic. The hydrolysis of the cation acids leads to the formation of either molecular products or complex ions. Equilibrium is established because these products are bases corresponding to the cation acids. Ammonium ions interact with water to form hydronium ions in equilibrium with molecular ammonia.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$
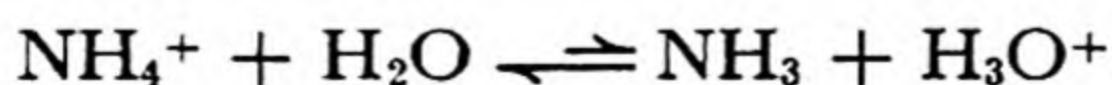
In the competition for protons, ammonia is the stronger base and the percentage of hydrolysis is small. The concentration of hydronium ions in a 0.1 molar solution of ammonium chloride at 20° is 7.5×10^{-6} molar.

Many hydrated cations, such as the cupric ion, undergo hydrolysis to produce acidic solutions.

$$Cu(H_2O)_4^{++} + H_2O \rightleftharpoons Cu(H_2O)_3(OH)^+ + H_3O^+$$
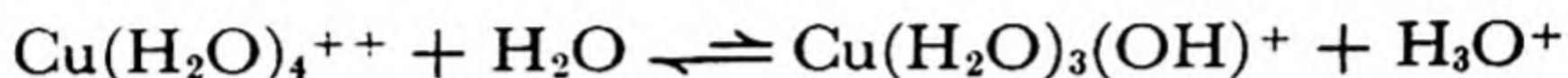
This is merely the ionization reaction of this acid. Although the complex cation formed is amphoteric, it does not hydrolyze further in a solution containing the increased concentration of hydronium ions required for equilibrium in the primary ionization. No precipitate of cupric hydroxide is formed by the hydrolysis of the cupric salts of the strong acids, even though this substance has very low solubility, unless the hydronium concentration is reduced by the addition of a stronger base. A large number of the metal ions hydrolyze to an appreciable degree.

Hydrolysis of Cation Acids and Anion Bases. The two effects, discussed separately in the preceding paragraphs, may occur simultaneously in a single solution if the positive ions of the salt are cations of weak bases, and the negative ions are the anions of weak acids. An acidic solution is required for the equilibrium of the cations with water, but the reaction of hydronium ions with the anions keeps the acidity low. Equilibrium cannot exist in such solutions until the concentrations of the salt ions have become low. Therefore, the degree of hydrolysis is relatively great. If the acidic and basic properties of the two ions are equal, the solution is neutral, but if the two are of unequal strength, the concentration of hydronium ions depends on the relative strength of the acid and the base formed. Ammonium carbonate yields acidic ammonium ions and basic carbonate ions.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$
$$CO_3^{--} + H_3O^+ \rightleftharpoons HCO_3^- + H_2O$$
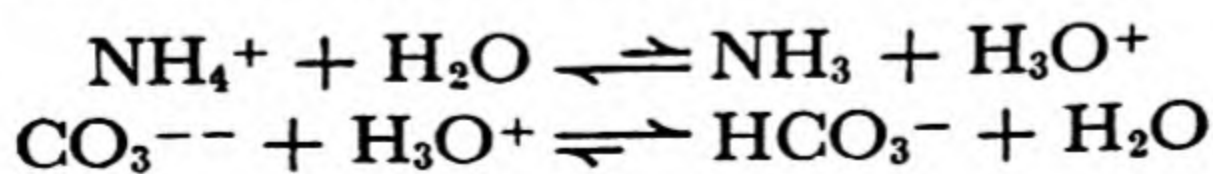
By combining these two effects, the following equation is obtained, showing the action of the cation acid and the anion base on each other in aqueous solution.

$$NH_4^+ + CO_3^{--} \rightleftharpoons NH_3 + HCO_3^+$$

The solution is basic because ammonia is more actively basic than the bicarbonate ion is acidic.

Degree of Hydrolysis of Salts. The percentage change in the concentration of the ions of a salt, caused by reaction with water, is the degree of hydrolysis. Usually, *the degree of hydrolysis of salts is small* and is affected by changes in conditions. The degree of hydrolysis depends on the properties of the ions and of the products formed by their reaction with water. The more weakly ionized the acid or the base formed during the reaction, the greater is the degree of hydrolysis. The low solubility of a product plays a part in determining the degree of hydrolysis.

A consideration of the equilibria involved in a solution of potassium cyanide illustrates the relationships upon which the degree of hydrolysis depends. The equation representing the hydrolysis of the cyanide ion is:

$$H_2O + CN^- \rightleftharpoons HCN + OH^-$$
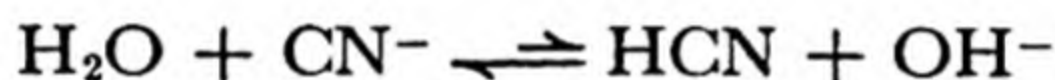
The equilibrium constant for this system is shown by the formula:

$$\frac{[HCN] \times [OH^-]}{[CN^-]} = K_{hydrolysis} \qquad (1)$$

The concentrations of the hydroxide and hydronium ions in aqueous solutions are related as shown by the ionization constant of water.

$$[H_3O^+] \times [OH^-] = K_{water}$$

$$[H_3O^+] = \frac{K_{water}}{[OH^-]} \qquad (2)$$

The relationship of the concentrations of the hydronium and cyanide ions is shown by the ionization constant of hydrocyanic acid:

$$\frac{[H_3O^+] \times [CN^-]}{[HCN]} = K_{HCN}$$

$$[H_3O^+] = \frac{K_{HCN} \times [HCN]}{[CN^-]} \qquad (3)$$

The concentration of hydronium ions shown by Equation (2) is identical with that shown by Equation (3).

$$\frac{K_{HCN} \times [HCN]}{[CN^-]} = \frac{K_{water}}{[OH^-]} \qquad (4)$$

By rearrangement of terms this equation is expressed in the form:

$$\frac{[HCN] \times [OH^-]}{[CN^-]} = \frac{K_{water}}{K_{HCN}} = K_{hydrolysis} \qquad (5)$$

The degree of hydrolysis depends on the ratio of the ionization constant of water to the ionization constant of the weak electrolyte the formation of which causes hydrolysis. In the simple case, the hydrolysis constant is equal to this ratio. If more than one weak electrolyte is formed, the relationship is more complex.

The hydrolysis of ions is virtually complete if one of the products is slightly soluble. Bismuth trichloride yields the hydrated bismuth ion in solution. This ion is a cation acid with an oxidation number of 3 +, and its hydroxy complexes are so weakly basic that hydrolysis proceeds to the secondary stage, forming the bismuthyl ion BiO^+, which combines with chloride ions to form the slightly soluble bismuthyl chloride, $BiOCl$. In order to simplify the equations, water of hydration may be omitted.

$$Bi^{+++} + H_2O + Cl^- \rightleftharpoons BiOCl \downarrow + 2 H^+$$
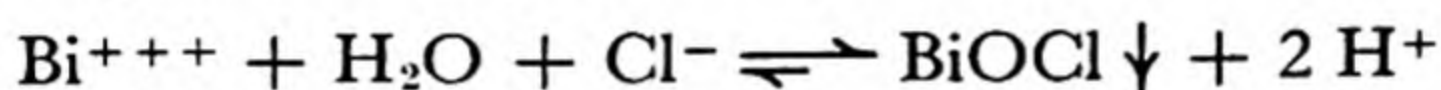
Although this reaction is almost complete, the addition of an excess of a strong acid causes the precipitate to dissolve. Antimony trichloride gives a similar result when it is dissolved in water.

The hydrolysis reaction is complete and irreversible if both products are slightly ionized and also slightly soluble. Aluminum sulfide is a slightly soluble salt yielding low concentrations of hydrated aluminum ions and sulfide ions. Hydrolysis of the cation acid produces the slightly soluble aluminum hydroxide, and the anion base produces the slightly soluble hydrogen sulfide. Consequently, the concentration of neither hydronium nor hydroxide ions can become great enough to meet the equilibrium requirements, and the decomposition of the salt is complete. The equation for the reaction, simplified by the omission of water of hydration from the formulas, is:

$$Al_2S_3 \downarrow + 6 H_2O \longrightarrow 2 Al(OH)_3 \downarrow + 3 H_2S \uparrow$$
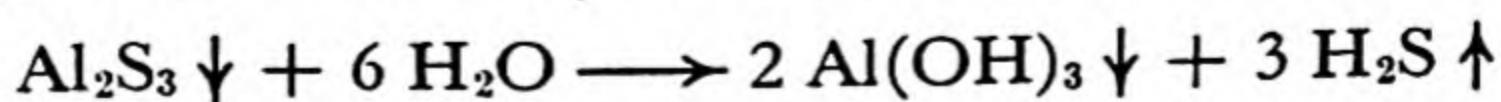
The sulfides and carbonates of aluminum, ferric iron, and chromium are not obtained by precipitation in aqueous solution.

The degree of hydrolysis may be increased by dilution. If the reaction is due to the formation of a single weak electrolyte in solution, dilution affects the ratio between the concentrations of the reacting

materials, shown in Equation (5), page 282. This in turn requires further hydrolysis to restore equilibrium. If, however, both the acid and the base produced during hydrolysis are weak and have approximately the same strength, the addition of water affects the concentrations of all significant ions to the same degree and does not change the ratio. Therefore, in such instances, the extent of hydrolysis is not affected by dilution.

Changing the concentration of one of the ions involved in the reaction, by the addition of a strong electrolyte that produces an ion in common, alters the degree of hydrolysis. The addition of ammonium chloride increases the degree of hydrolysis of ammonium carbonate.

$$NH_4^+ + CO_3^{--} \rightleftharpoons NH_3 + HCO_3^-$$

A high concentration of hydroxide ions decreases the concentration of ammonium ions and, consequently, decreases the degree of hydrolysis.

The degree of hydrolysis is affected by changes in temperature. Water is more highly ionized at high than at low temperatures. The increased concentration of the ions of water increases the effects caused by these ions. The effect of a rise in temperature is especially great if molecular gases or products that are unstable toward heat are formed. The change in solubility resulting from the rise in temperature causes the completion of some hydrolytic reactions which are normally incomplete.

EXERCISES

1. What is the significance of acid and base in terms of (*a*) the Arrhenius theory of ionization, (*b*) the Lowry and Brönsted definitions?
2. Name three classes of acids, and give examples of each. Write equations to show an acid reaction of a member of each class.
3. Name two classes of bases, and give examples to illustrate each class. Write an equation showing a basic reaction of each of the substances you select as examples.
4. What is meant by corresponding acids and bases? Give examples to illustrate your definition. How does the strength of the base vary with the strength of the corresponding acid?
5. What are ampholytes? Write equations to show the amphoteric nature of several ampholytes.
6. How is the acidic or basic nature of an element's hydroxide explained in terms of atomic structures?
7. What two reactions may be used for the preparation of amphoteric hydroxides?

Illustrate each type of reaction by equations showing the formation of three different hydroxides.

8. What is meant by a neutral aqueous solution? What is the essential reaction of neutralization? What is meant by the heat of neutralization?

9. What is the nature of an indicator? Explain its changes in color.

10. What is a buffer solution? Explain the regulation of the hydronium ion concentration in such solutions.

11. What is meant by the hydrolysis of ions? What is the cause of hydrolysis?

12. Which types of ions hydrolyze to give basic solutions? Select an example in which the reaction is incomplete and explain why (a) the solution is basic, and (b) the reaction is incomplete.

13. Select an example of incomplete hydrolysis that gives an acidic solution and explain why (a) the solution is acidic and (b) the reaction is incomplete.

14. What is meant by the degree of hydrolysis? What determines the degree of hydrolysis?

15. What changes in conditions affect the degree of hydrolysis? Explain the effect of each and illustrate by examples.

16. Under what conditions is the hydrolysis of ions virtually complete? Select an example and explain the fact that hydrolysis is virtually complete. How may the reaction be reversed? Explain.

17. Select an example of hydrolysis that is complete and irreversible. Explain why the reaction is irreversible.

18. What is a buffer solution? How are changes in the hydronium ion concentration prevented in buffer solutions?

SUPPLEMENTARY READINGS

Hildebrand, J. H., *Principles of Chemistry*, The Macmillan Company, New York, 1940, pp. 175–82.

Hammett, L. P., *Solutions of Electrolytes*, McGraw-Hill Book Company, Inc., New York, 1936, chap. IV.

Bjerrum, N., *Inorganic Chemistry*, trans. R. P. Bell, William Heinemann, Ltd., London, 1936, pp. 88–130.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, American Book Company, New York, 1936, chap. XI.

Hogness, T. R., and W. C. Johnson, *Qualitative Analysis and Chemical Equilibrium*, Henry Holt and Company, Inc., New York, 1937, chaps. VI, VIII.

Bjerrum, N., "Acids, Salts, and Bases," *Chemical Reviews* **16**, 287 (1935).

Hall, N. F., "Systems of Acids and Bases," *J. Chem. Education* **17**, 124 (1940).

Hammett, L. P., "The Theory of Acids and Bases in Analytical Chemistry," *J. Chem. Education* **17**, 131 (1940).

Foster, L. S., "Hydrolysis and Its Relation to Ionic Charge and Radius," *J. Chem. Education* **17**, 509 (1940).

Chapter 18

ANALYTICAL SEPARATIONS
OF THE METAL IONS

The solubilities of different substances in water vary greatly. In a mixture containing a number of substances, individual ions may be separated and detected by procedures based on these differences in solubility. At first groups of ions are separated on the basis of similarities in solubility. Specific differences between the members of each group are then utilized to complete the separation and detection of the individual ions.

Qualitative analysis involves procedures that cause separations sufficiently complete to permit the positive identification of the ions present in the solution, and to prevent interferences in subsequent tests. *Quantitative analysis* involves the determination of the amounts or concentrations of specific substances. The important principles that make these procedures rational are studied in analytical chemistry. Among these principles, solubility product, common ion effect, hydrolysis, and complex ion formation are notable.

This chapter treats the application of these principles to typical separations in qualitative analysis. The specific separations and tests are not described in detail. Knowledge of specific procedures and observations is best gained in laboratory practice.

The Solubility Product Principle. The solubility products of the chlorides of silver, mercurous, and lead ions are small.

$$[Ag^+] \times [Cl^-] = 1.1 \times 10^{-10}$$
$$[Hg_2^{++}] \times [Cl^-]^2 = 3 \times 10^{-18}$$
$$[Pb^{++}] \times [Cl^-]^2 = 1.8 \times 10^{-4}$$

When hydrochloric acid is added to a solution containing these ions, the ion concentration product for each ion is greater than the solubility product, *e.g.*, for silver chloride:

$$[Ag^+] \times [Cl^-] > 1.1 \times 10^{-10}$$

Consequently, precipitation occurs, lowering the ion concentrations sufficiently to bring them into accord with the respective solubility products.

$$Ag^+ + Cl^- \rightleftharpoons AgCl \downarrow$$
$$Hg_2^{++} + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 \downarrow$$
$$Pb^{++} + 2\,Cl^- \rightleftharpoons PbCl_2 \downarrow$$
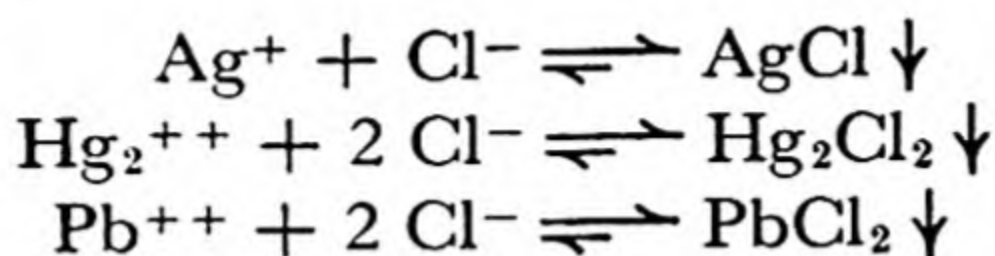
It is apparent from the solubility product of lead chloride that moderate concentrations of lead ions remain in solution in equilibrium with the precipitate. The solubility products of the other common chlorides are great enough so that the ion concentration products are below the solubility products.

$$[Hg^{++}] \times [Cl^-]^2 < S_{HgCl_2}$$

No special regulation of concentration is required to effect a separation between the chlorides of these ions, known as the silver group ions, and of the other common metal ions.

Regulation of Ion Concentrations. In many instances, ion concentrations must be regulated in order to effect a desired separation, because the differences in solubility are small. A method of maintaining a regulated low concentration of ions is based frequently on the common ion effect. A weak electrolyte, which furnishes the required ions, is used as the precipitant in the presence of a strong electrolyte that furnishes an ion common to the weak electrolyte. The high concentration of the ion common to both substances not only decreases the concentration of the other ion supplied by the weak electrolyte, but also prevents any significant increase in the concentration of this ion, if it is liberated during the reaction. The high concentration of the molecular weak electrolyte serves as a source of supply preventing a significant decrease in the concentration of the precipitant as the reaction proceeds. Thus, relatively large amounts of a precipitate may be formed even though the concentration of the ions involved in the reaction is maintained at a low level. Complex ion formation and hydrolysis provide other reactions by which ion concentrations may be regulated.

Regulation of the Concentration of Hydrogen Ions. Although in analytical procedures hydrogen ions do not enter directly into the formation of many precipitates, the concentration of this ion

is important in its effect on other ions supplied by weak acids. A solution of a weak acid containing a high concentration of one of its salts is a *buffer solution*. (See page 277.) The separation of barium and strontium ions in a solution free from interfering ions is an application of buffer solutions. The separation is based on differences in the solubility of chromates and on the regulation of the chromate ion concentration.

$$[Ba^{++}] \times [CrO_4^{--}] > S_{BaCrO_4} = 2 \times 10^{-10}$$
$$[Sr^{++}] \times [CrO_4^{--}] < S_{SrCrO_4} = 5 \times 10^{-5}$$

The concentration of chromate ions required to establish this condition may be secured through the use of a weakly acidic solution of potassium chromate. Chromate ions react with hydrogen ions in the reversible reaction:

$$2\,CrO_4^{--} + 2\,H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$
$$\frac{[CrO_4^{--}] \times [H^+]^2}{[Cr_2O_7^{--}]} = K$$
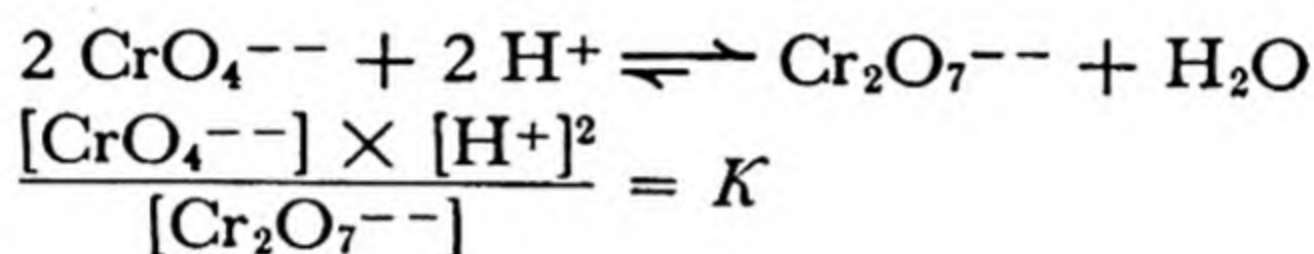
If the hydrogen ion concentration is high, the chromate ion concentration is too low to cause the precipitation of barium chromate. If the hydrogen ion concentration is too low, the chromate ion concentration may be great enough to cause at least partial precipitation of strontium chromate. Hence, a solution containing a regulated low concentration of hydrogen ions is required. A dilute solution of acetic acid, containing sodium acetate, gives a satisfactory concentration of hydrogen ions for this purpose.

$$H^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2$$
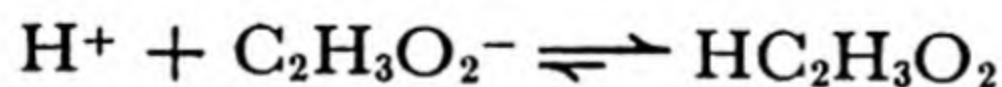
Under these conditions, the chromate ion concentration is sufficiently great to precipitate barium chromate but not strontium chromate, and the available source of chromate ions — from the high concentration of the dichromate — is great enough to insure practically complete precipitation of relatively large quantities of barium chromate.

Regulation of the Concentration of Hydroxide Ions. The hydroxide and hydrogen ion concentrations are regulated as defined by the ionization constant of water.

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$

The regulation of the concentration of one of these ions in solution automatically regulates the concentration of the other. In acidic solutions, however, the concentration of hydroxide ions is too low to cause precipitation of the hydroxides of many metals. Ammonia is the only common soluble base that gives weakly basic solutions.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$
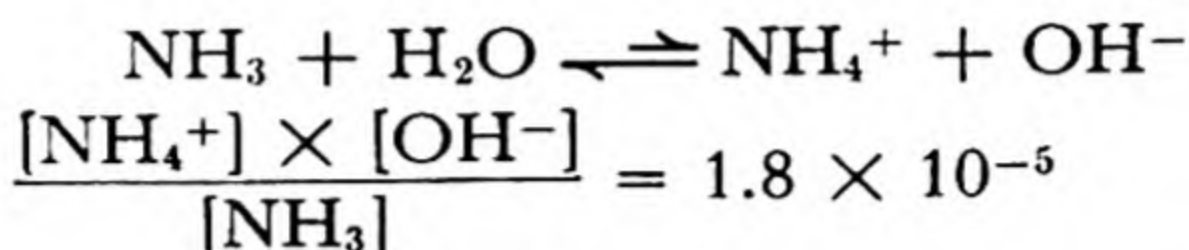
Low concentrations of hydroxide ions may be obtained through the use of solutions of ammonia containing ammonium chloride. Using these reagents the concentrations of hydroxide ions may be regulated so as to cause the precipitation of aluminum hydroxide but not magnesium hydroxide.

$$[Al^{+++}] \times [OH^-]^3 > 1.9 \times 10^{-33}$$
$$[Mg^{++}] \times [OH^-]^2 < 2.8 \times 10^{-11}$$
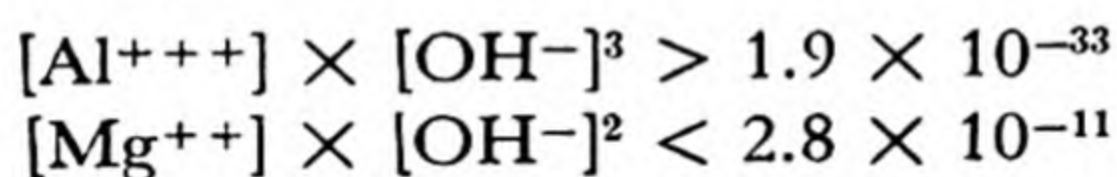
Ferric hydroxide and chromic hydroxide may also be precipitated under these conditions. Ferric, aluminum, and chromic ions are members of the iron group of cations.

A second reason for the use of weakly basic solutions in precipitating the hydroxides of the ions of the iron group from solution, is based on the amphoteric nature of these hydroxides. Aluminum and chromic hydroxides are dissolved by a high concentration of hydroxide ions. The total concentration of dissolved aluminum compounds in aqueous solution is equal to the sum of the concentrations of the different cations and anions containing this element. In acidic solution, the hydrated aluminum ions, $Al(H_2O)_6^{+++}$, predominate. As the concentration of hydrogen ions is decreased by the addition of a base, hydroxide complex ions are first formed and then the hydroxide precipitates. The concentration of cations decreases during the precipitation of the hydroxide, and the total solubility decreases likewise. There is little change in the concentration of complex anions so long as the solution is acidic. This condition is represented along AB in Fig. 89. The concentration of cations is very low when the solution is slightly basic. As the concentration of hydroxide ions is increased, large proportions of aluminum hydroxide are converted into complex anions. This

condition is represented along *BC*. The point *B* represents that concentration of hydroxide ions which gives the most nearly complete precipitation of alu-
minum hydroxide. This point is known as the isoelectric point, because it represents the concentrations of ions at which the acidic and basic properties of the amphoteric hydroxide are equal. This is the most favorable condition for the precipitation of the hydroxide. The solution of ammonia containing ammo-

Fig. 89

nium chloride gives an hydroxide concentration near the value for the isoelectric point for the hydroxides of aluminum, chromic, and ferric ions.
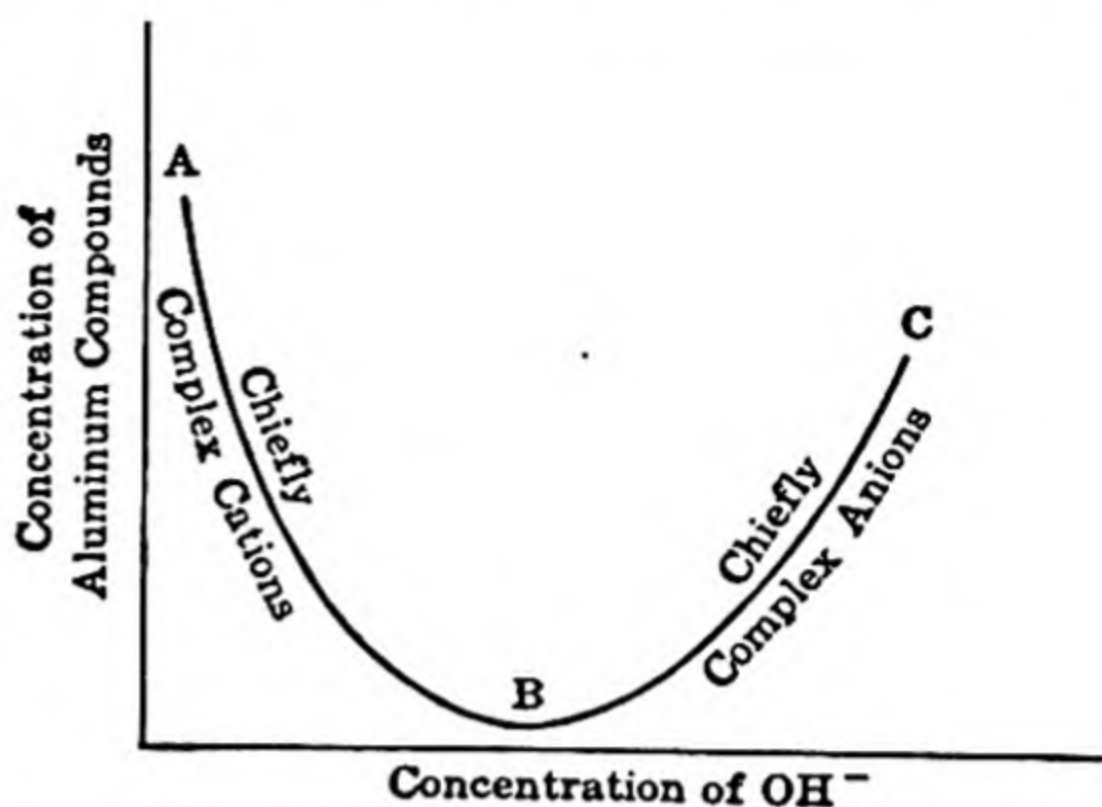
Regulation of the Concentration of Sulfide Ions. Hydrogen sulfide is a weak electrolyte which has low solubility in water. The relation between the hydrogen and sulfide ion concentrations in a saturated solution of this gas is represented by the following equation.

$$H_2S \rightleftharpoons 2 H^+ + S^{--}$$
$$[H^+]^2 \times [S^{--}] = K = 1.1 \times 10^{-23}$$
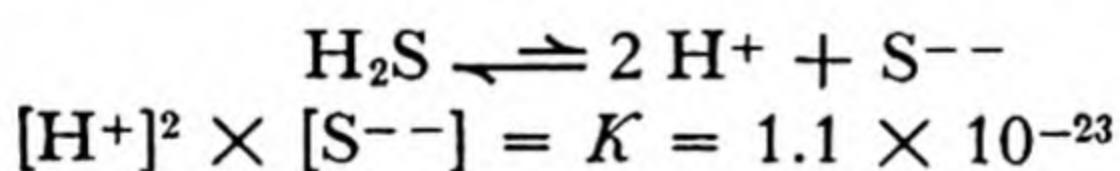
The concentration of sulfide ions varies inversely with the square of the hydrogen ion concentration. Consequently, the concentration of sulfide ions may be varied greatly and also may be controlled within narrow limits by regulating the concentration of hydrogen ions.

Since metal sulfides differ greatly in solubility, hydrogen sulfide is used extensively in qualitative analysis to cause the separation of metal ions. Lead and manganous ions, for example, may be separated through the use of hydrogen sulfide as a precipitant. The solubility product of lead sulfide is approximately 1×10^{-29}, and of manganous sulfide, 1.6×10^{-16}. In a saturated solution of hydrogen sulfide, in which the hydrogen ion concentration is made 0.3 M. by the addition of a strong acid, the concentration of sulfide ions is only about 1.2×10^{-22} M. This concentration

of sulfide ions is great enough to cause the precipitation of lead sulfide but not of manganous sulfide.

$$[Pb^{++}] \times [S^{--}] > 1 \times 10^{-29}$$
$$[Mn^{++}] \times [S^{--}] < 1.6 \times 10^{-16}$$

There are a number of metal ions yielding precipitates in solutions of 0.3 M. hydrogen ion concentration. There are also a number of cations which fail to produce precipitates under these conditions.

The concentration of sulfide ions may be increased by reducing the concentration of hydrogen ions. In a solution containing ammonium chloride and a moderate excess of ammonia, saturated with hydrogen sulfide, the concentration of sulfide ions is sufficiently great to cause the precipitation of the sulfides of nickel, cobalt, manganese, and zinc. Even in basic solutions, the concentration of sulfide ions is not great enough to precipitate the sulfides of magnesium, barium, strontium, and calcium.

Sulfides having low solubility may be dissolved by decreasing the concentration of sulfide ions so greatly that the product of the ion concentrations is less than the solubility product of the specific compound. Many sulfides may be dissolved by dilute hydrochloric acid, e.g., ferrous, manganous, and zinc sulfides.

$$MnS + 2 H^+ \longrightarrow Mn^{++} + H_2S \uparrow$$
$$[Mn^{++}] \times [S^{--}] < 1.6 \times 10^{-16}$$
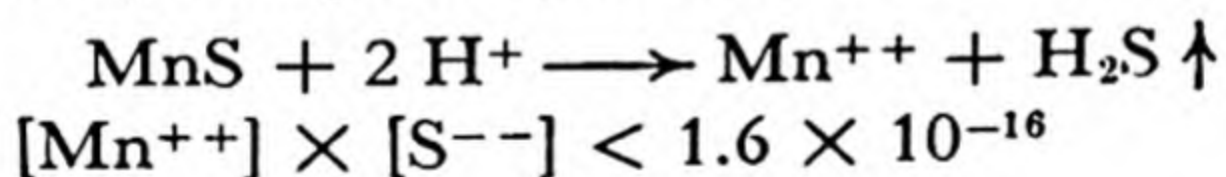
Other sulfides require the action of more concentrated hydrochloric acid, e.g., antimony, stannous, and cadmium sulfides.

$$CdS + 2 H^+ \longrightarrow Cd^{++} + H_2S \uparrow$$
$$[Cd^{++}] \times [S^{--}] < 1.4 \times 10^{-28}$$
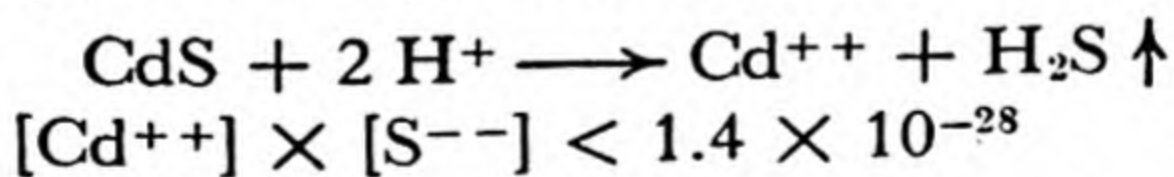
Still other sulfides are not readily dissolved by the action of hydrochloric acid, but may be dissolved by dilute nitric acid, e.g., copper, lead, and bismuth sulfides. The solubility of these sulfides is so low that hydrochloric acid does not significantly affect the concentration of sulfide ions in equilibrium with the precipitates. The oxidizing action of nitric acid converts sulfide ions into free sulfur, thus decreasing the concentration of this ion to a lower value than required for equilibrium with the solid sulfides. The derivation of the equation for this reaction, in terms of electronic changes involved, is developed subsequently on page 351.

$$3\,CuS + 8\,H^+ + 2\,NO_3^- \longrightarrow 3\,Cu^{++} + 3\,S + 2\,NO + 4\,H_2O$$
$$[Cu^{++}] \times [S^{--}] < 4 \times 10^{-38}$$
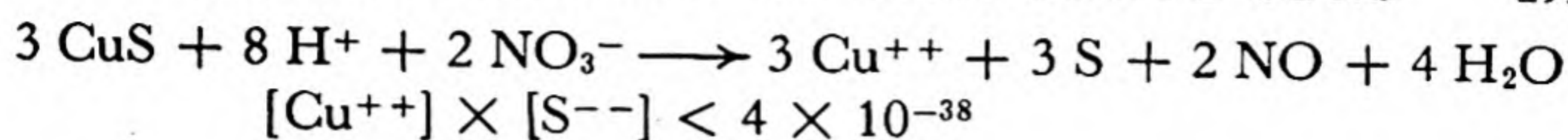
Regulation of the Concentration of Carbonate Ions. A number of the metal ions yield insoluble precipitates by reaction with solutions of carbonates. With the exception of the ions of barium, strontium, calcium, and magnesium, the cations which yield slightly soluble carbonates are separated before the carbonate group is precipitated. The carbonates must be precipitated in basic solution, because they are decomposed in acidic solutions with the evolution of carbon dioxide. The solubility products of the carbonates of barium, strontium, calcium, and magnesium are:

$$[Ba^{++}] \times [CO_3^{--}] = 6.2 \times 10^{-10}$$
$$[Sr^{++}] \times [CO_3^{--}] = 4.6 \times 10^{-9}$$
$$[Ca^{++}] \times [CO_3^{--}] = 2 \times 10^{-8}$$
$$[Mg^{++}] \times [CO_3^{--}] = 1 \times 10^{-5}$$
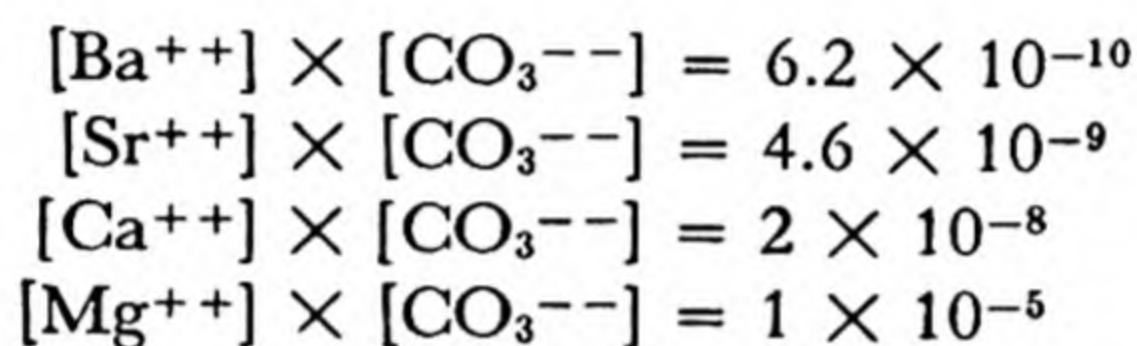
The carbonates of barium, strontium, and calcium may be precipitated as the calcium group of cations — leaving magnesium ions in the solution — by the use of reagents that furnish a regulated low concentration of carbonate ions.

$$[Sr^{++}] \times [CO_3^{--}] > 4.6 \times 10^{-9}$$
$$[Mg^{++}] \times [CO_3^{--}] < 1 \times 10^{-5}$$
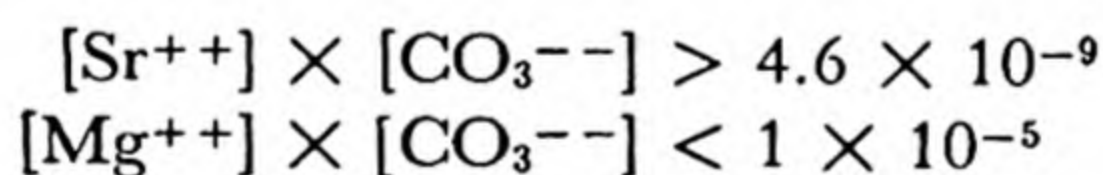
Although the solution must be basic, the concentration of hydroxide ions must be so low that magnesium hydroxide will not be precipitated.

$$[Mg^{++}] \times [OH^-]^2 < 2.8 \times 10^{-11}$$
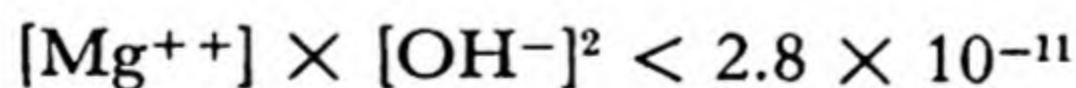
Ammonium carbonate yields a low concentration of carbonate ions, because it is composed of the acidic ammonium ion and the basic carbonate ion. In aqueous solution, these ions react to form ammonia and bicarbonate ions to such a degree that the concentration of carbonate ions at equilibrium in 0.1 M. solution is only 0.024 M.

$$NH_4^+ + CO_3^{--} \rightleftharpoons NH_3 + HCO_3^-$$
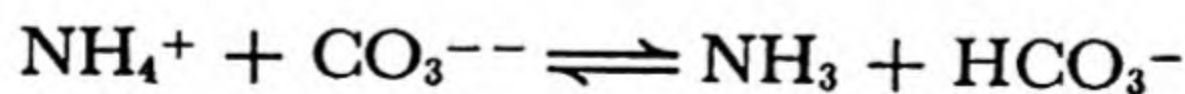
The proper adjustment of these ion concentrations is secured by adding ammonia and ammonium chloride as well as ammonium carbonate. The presence of ammonia in the solution leads to an

increased concentration of hydroxide ions. The hydroxide ion concentration does not become sufficiently great to cause precipitation of magnesium hydroxide in the presence of an excess of ammonium ions from the ammonium chloride.

Analytical Applications of Hydrolysis. The adjustment of the carbonate ion concentration in a solution of ammonium carbonate involves the equilibrium of each of its ions with water, in addition to the direct reaction of ammonium ions with carbonate ions. Many of the metal ions are hydrated in solution. In a number of instances, these ions are hydrolyzed to give acidic solutions.

Evaporation of solutions to remove excessive concentrations of certain ions, such as ammonium ions, is required at different stages in the analysis. During evaporation, the degree of hydrolysis of some of the metal ions may become great enough to cause errors if not corrected. Hydrated magnesium ions have only weak acidic properties in aqueous solution.

$$Mg^{++} + H_2O \rightleftharpoons Mg(OH)^+ + H^+$$
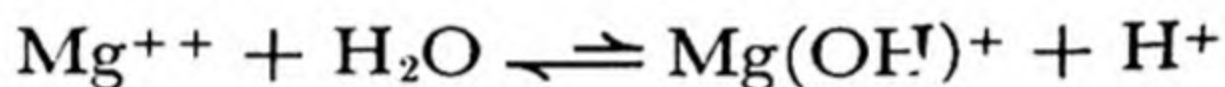
As the solution is evaporated and the temperature of the solution becomes higher, the degree of hydrolysis increases. Hydrogen ions are removed from solution through the evaporation of hydrogen chloride along with water vapor.

$$H^+ + Cl^- \longrightarrow HCl \uparrow$$
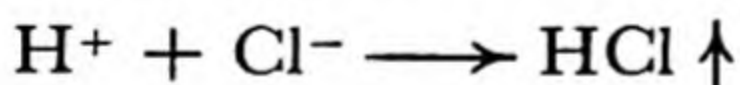
Under these conditions, the hydrolytic reaction proceeds to completion, producing a dry residue consisting of magnesium oxide and magnesium hydroxychloride.

$$Mg(OH)^+ + H_2O \rightleftharpoons Mg(OH)_2 \downarrow + H^+$$
$$Mg(OH)_2 \longrightarrow MgO + H_2O \uparrow$$
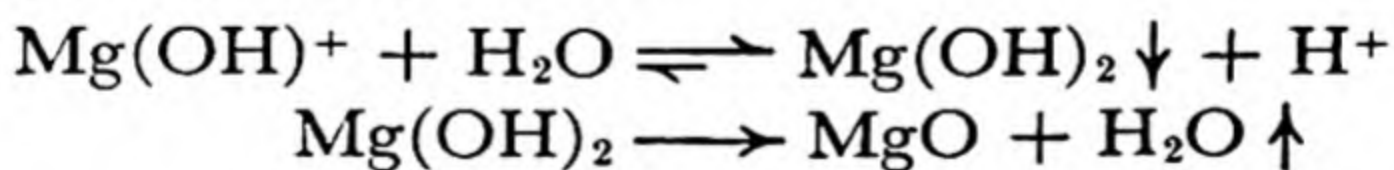
This product is not soluble in water, and such residues must be extracted with acid to bring the ions back into the solution.

Analytical Applications of Complex Ion Formation. Conditions leading to the formation of complex ions, and the effects on the concentrations of simple ions are discussed in Chapter 16, page 257. The behavior of complex ions is similar to that of other weakly ionized, soluble products. Consequently, complex ion formation may be applied as a means of regulating ion concentrations. The reduction in the concentrations of simple ions so produced

in some instances may cause the dissolving of precipitates and in other instances may prevent precipitation.

Ammonia Complex Ions. The separation of silver and mercurous ions may be accomplished by the reaction of ammonia with a precipitate of these two chlorides.

$$AgCl \downarrow + 2\,NH_3 \longrightarrow Ag(NH_3)_2{}^+ + Cl^-$$
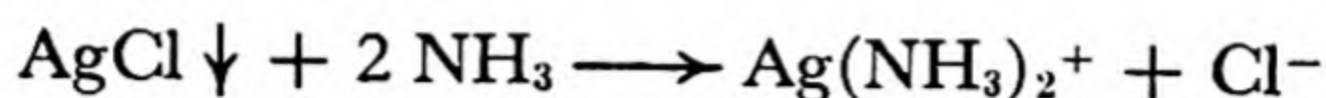
Mercurous chloride reacts with ammonia to form a mixture of two insoluble products, free mercury and mercuric amido chloride.

$$Hg_2Cl_2 + 2\,NH_3 \longrightarrow HgNH_2Cl \downarrow + Hg \downarrow + NH_4{}^+ + Cl^-$$
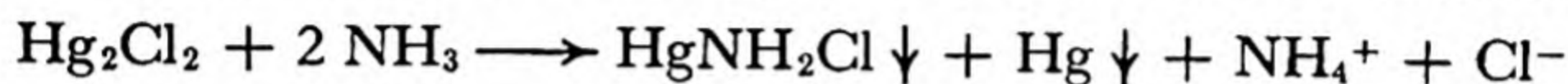
The separation of copper and cadmium ions from bismuth during the analysis of the copper group depends on the formation of complex metal ammonia ions.
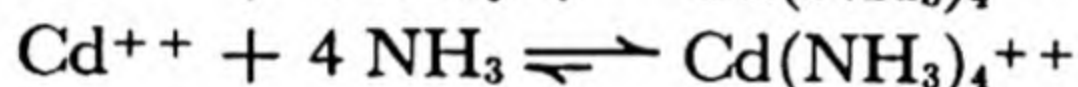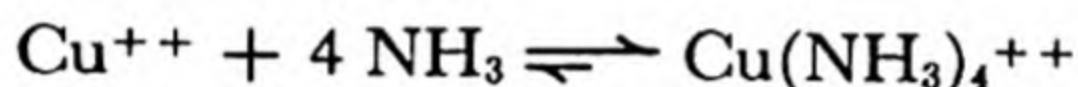
$$Cu^{++} + 4\,NH_3 \rightleftharpoons Cu(NH_3)_4{}^{++}$$
$$Cd^{++} + 4\,NH_3 \rightleftharpoons Cd(NH_3)_4{}^{++}$$

The concentrations of the simple metal ions are so greatly reduced that

$$[Cu^{++}] \times [OH^-]^2 < S_{Cu(OH)_2}$$
$$[Cd^{++}] \times [OH^-]^2 < S_{Cd(OH)_2}$$

Bismuth does not form a complex ion with ammonia, and the hydroxide is slightly soluble.

$$[Bi^{+++}] \times [OH^-]^3 > S_{Bi(OH)_3}$$
$$Bi^{+++} + 3\,OH^- \rightleftharpoons Bi(OH)_3 \downarrow$$
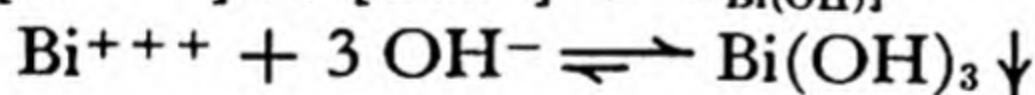
Nickel, cobalt, and zinc ions yield ammonia complex ions in ammoniacal solution.

$$Ni^{++} + 6\,NH_3 \rightleftharpoons Ni(NH_3)_6{}^{++}$$
$$Co^{++} + 6\,NH_3 \rightleftharpoons Co(NH_3)_6{}^{++}$$
$$Zn^{++} + 4\,NH_3 \rightleftharpoons Zn(NH_3)_4{}^{++}$$
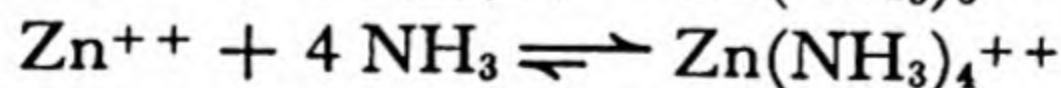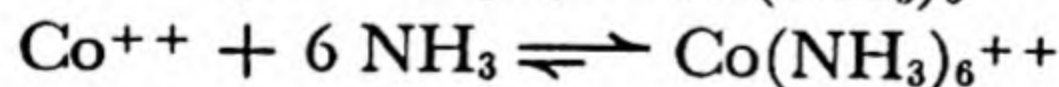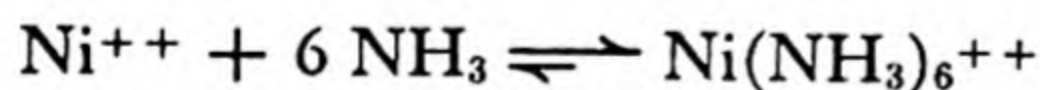
The concentrations of the simple metal ions are so greatly reduced by these reactions that the hydroxides do not precipitate in solutions containing an excess of ammonia.

Hydroxide Complex Ions. Some analytical separations are based on the amphoteric nature of the hydroxides, *e.g.*, the separation of zinc and manganous ions in the nickel group. Zinc and manganous hydroxides are precipitated by adding a slight excess of sodium hydroxide to a solution of these ions.

$$Mn^{++} + 2\,OH^- \rightleftharpoons Mn(OH)_2 \downarrow$$
$$Zn^{++} + 2\,OH^- \rightleftharpoons Zn(OH)_2 \downarrow$$
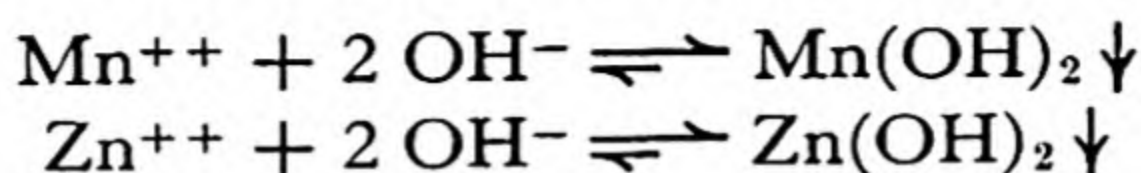
Zinc hydroxide is amphoteric and, consequently, reacts with an excess of hydroxide ions to form the hydroxide complex ion, called the zincate ion.

$$Zn(OH)_2 + 2\,OH^- \rightleftharpoons Zn(OH)_4^{--}$$
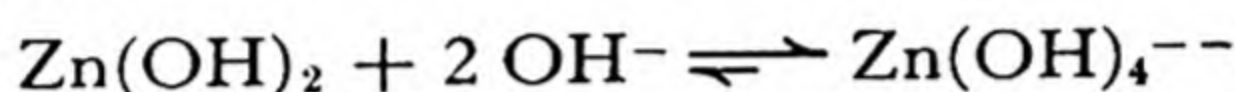
The concentration of zinc ions is reduced so greatly that the precipitate dissolves.

$$[Zn^{++}] \times [OH^-]^2 < S_{Zn(OH)_2}$$

Manganous hydroxide is not amphoteric. Consequently, the concentration of the manganous ion is not significantly affected, and this hydroxide does not dissolve.

$$[Mn^{++}] \times [OH^-]^2 = S_{Mn(OH)_2}$$

The same principle may be applied in the separation of aluminum and ferric hydroxides. Aluminum hydroxide is active enough to react with a solution of sodium hydroxide, but ferric hydroxide does not react, unless the concentration of sodium hydroxide is large.

Sulfide Complex Ions. Sulfide ions readily add other atoms and ions producing complex ions. The simplest of these is the disulfide ion, formed by the reaction of sulfide ions and sulfur atoms in basic solution.

$$S^{--} + S \rightleftharpoons S_2^{--}$$

Additional atoms of sulfur may become attached to this ion to form more complex structures, which have the same electrovalence as the simple sulfide ion. Solutions containing such complex sulfide ions are called *polysulfide* solutions.

The sulfides of arsenic, antimony, and stannic tin add sulfide ions to form complex *thio* ions. The solubilities of these sulfides are so small that the concentrations of their ions in saturated solutions are very low.

$$As_2S_3 \downarrow \rightleftharpoons 2\,As^{+++} + 3\,S^{--}$$
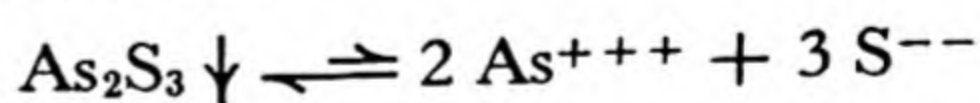
The thioarsenite is formed by reaction with an excess of sulfide ions, thus reducing the concentration of the arsenic ion enough to cause the precipitate to dissolve.

$$[As^{+++}]^2 \times [S^{--}]^3 < S_{As_2S_3}$$
$$As_2S_3 \downarrow + 3\,S^{--} \rightleftharpoons 2\,AsS_3^{---}$$
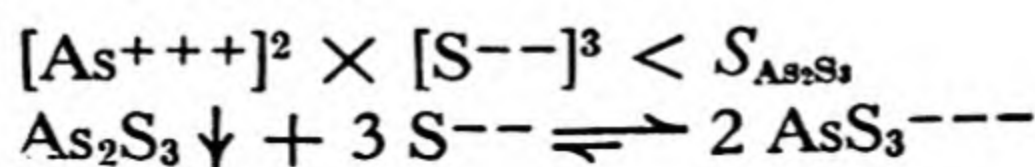
Antimony sulfide and stannic sulfide react in a similar manner with sulfide ions to form the thioantimonite, SbS_3^{---}, and thiostannate, SnS_3^{--}, respectively. Stannous sulfide, however, does not produce a complex anion with simple sulfide ions, but it does react with solutions containing polysulfide ions to form the thiostannate.

$$SnS\downarrow + S_2^{--} \longrightarrow SnS_3^{--}$$
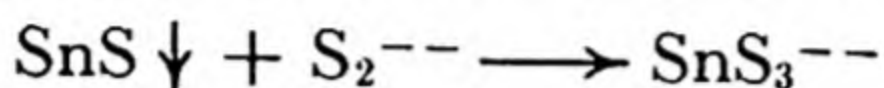
Furthermore, arsenic and antimony sulfides are converted into thioarsenate and thioantimonate, respectively, by the action of the polysulfide.

$$As_2S_3\downarrow + 2\,S_2^{--} + S^{--} \longrightarrow 2\,AsS_4^{---}$$
$$Sb_2S_3\downarrow + 2\,S_2^{--} + S^{--} \longrightarrow 2\,SbS_4^{---}$$
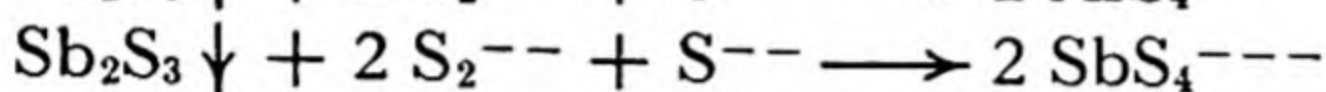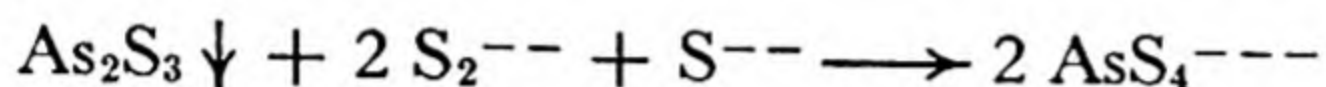
The sulfides of arsenic, antimony, and tin may be recovered in the solid state by adding a moderate excess of hydrochloric acid to the solution of the thio salts. The complex ions are decomposed by the acid, with the evolution of hydrogen sulfide and the reprecipitation of the simple sulfides.

$$SnS_3^{--} + 2\,H^+ \longrightarrow SnS_2\downarrow + H_2S\uparrow$$
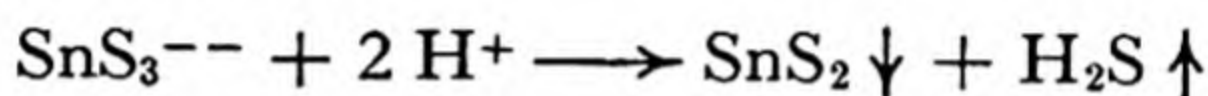
Cyanide Complex Ions. The cyanide ion reacts with a number of the metal ions to form cyanide complex ions, *e.g.*, $Ag(CN)_2^-$, $Cd(CN)_4^{--}$, $Zn(CN)_4^{--}$, $Fe(CN)_6^{----}$. As in the formation of other complex ions, the concentrations of the simple ions are reduced so greatly that slightly soluble compounds are dissolved. Thus, silver iodide, which does not dissolve in ammonia solutions, is dissolved by a solution of potassium cyanide.

$$AgI\downarrow \rightleftharpoons Ag^+ + I^-$$
$$[Ag^+] \times [I^-] = S_{AgI} = 8.5 \times 10^{-17}$$
$$Ag^+ + 2\,CN^- \rightleftharpoons Ag(CN)_2^-$$
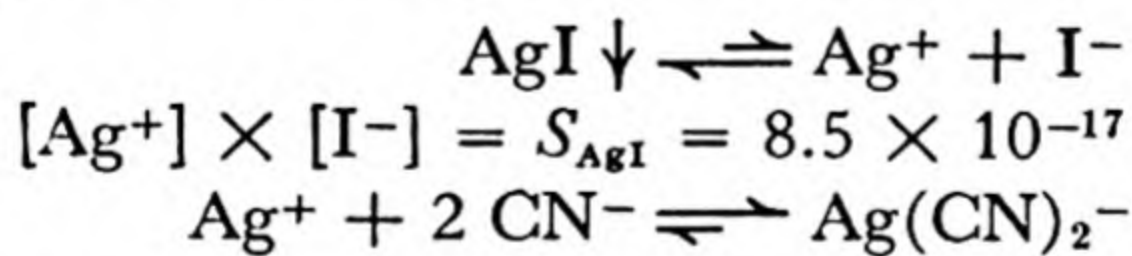
The concentration of silver ions is now below that required for equilibrium with the precipitate.

$$[Ag^+] \times [I^-] < S_{AgI}$$
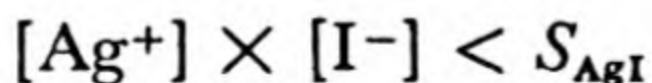
An application of complex cyanide ion formation is made in the separation of copper and cadmium ions. Both of these ions yield ammonia complex ions, and therefore, in the analysis of the copper group of ions, they are found together in the filtrate from the separation of bismuth hydroxide. These complex ammonia

ions are decomposed by cyanide ions, forming the more stable cyanide complex ions. The reaction of cyanide ions with cupric ammonia complex ions produces the cuprocyanide complex ion and free cyanogen, C_2N_2.

$$Cd(NH_3)_4^{++} + 4\ CN^- \rightleftharpoons Cd(CN)_4^{--} + 4\ NH_3$$
$$2\ Cu(NH_3)_4^{++} + 6\ CN^- \longrightarrow 2\ Cu(CN)_2^- + C_2N_2 \uparrow + 8\ NH_3$$
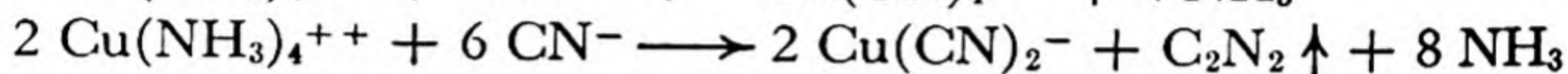
The stability of the cuprocyanide complex ion is so great that it does not yield a high enough concentration of cuprous ions to produce a precipitate of cuprous sulfide when hydrogen sulfide is passed into the solution. The cadmium cyanide complex is less stable, and it is decomposed by the action of hydrogen sulfide, forming a yellow precipitate of cadmium sulfide.

$$Cd(CN)_4^{--} + H_2S + 2\ OH^- \rightleftharpoons CdS \downarrow + 4\ CN^- + 2\ H_2O$$
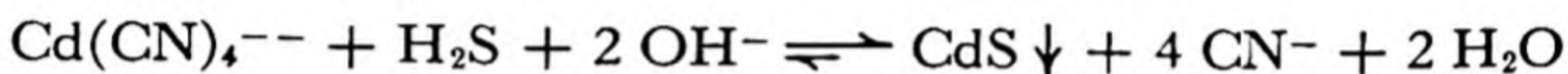
Other Complex Ions. Many of the metal ions are hydrated in aqueous solution, existing as complex hydrated ions. The water molecules are usually omitted from the symbols and formulas, except in considerations of acidity and basicity, in order to simplify the symbolism. Thus, cupric ions are commonly represented by Cu^{++}, in preference to $Cu(H_2O)_4^{++}$, and aluminum ions by Al^{+++}, in preference to $Al(H_2O)_6^{+++}$. A number of the anions are also complex, but are usually simplified in formulas, *e.g.*, $Al(OH)_4^-$ instead of $Al(H_2O)_2(OH)_4^-$.

There are a number of complex ions containing chloride and other halide ions. There is no evidence of the existence of free stannic ions, Sn^{++++}, in aqueous solution. It is more probable that in this oxidation state the ion of tin in hydrochloric acid solution is the chlorostannate ion, $SnCl_6^{--}$. Likewise, the ion of antimony in hydrochloric acid solution is probably $SbCl_6^{---}$. It is customary to use simple formulas for the representation of such complex ions, unless some special significance is attached to the formulation of the complex structure. The addition of a large excess of hydrochloric acid in the precipitation of the silver group of cations leads to incomplete precipitation. Both lead and silver may form chloride complex ions.

$$AgCl \downarrow + Cl^- \rightleftharpoons AgCl_2^-$$
$$PbCl_2 \downarrow + 2\ Cl^- \rightleftharpoons PbCl_4^{--}$$
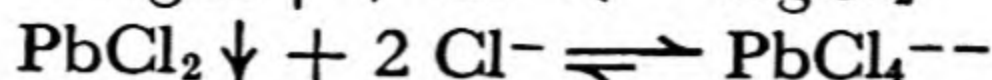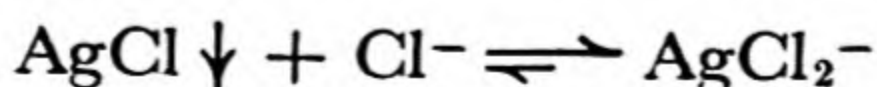
Cuprous chloride is very slightly soluble in water, but it dissolves in hydrochloric acid solutions to form the chlorocuprite ion, $CuCl_2^-$.

$$CuCl \downarrow + Cl^- \rightleftharpoons CuCl_2^-$$
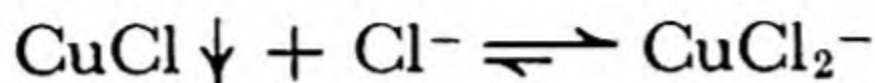
EXERCISES

1. What is qualitative analysis? What constitutes a satisfactory test for an ion?
2. What is meant by the solubility product of a substance? What are the conditions for the formation of a precipitate? the dissolving of a precipitate?
3. What conditions must be established for the separation of two ions that are together in solution?
4. What methods are used to regulate ion concentrations, so as to produce a separation when the difference in solubility products is relatively small?
5. How may a regulated low concentration of hydrogen ions be secured? In establishing conditions for precipitation, what advantage has a buffer solution over measured low concentrations of a strong acid?
6. Explain the effect of a low concentration of hydrogen ions in establishing conditions for the precipitation of relatively large amounts of barium chromate without precipitating strontium chromate.
7. How is a regulated low concentration of hydroxide ions secured? Explain an ion separation requiring the use of a weakly basic solution.
8. How is the concentration of sulfide ions regulated? Explain the application of hydrogen sulfide equilibria to the following: (a) the separation of the acid hydrogen sulfide group of cations from the basic hydrogen sulfide group; (b) the precipitation of the sulfides of the nickel group; (c) the solution of zinc sulfide in hydrochloric acid.
9. Explain why ammonium carbonate is used in preference to sodium carbonate for the precipitation of the carbonates of the ions of the calcium group.
10. Explain the application of the reaction of hydrolysis in the precipitation of the hydroxides of ferric, aluminum, and chromium ions in acidic solution.
11. Discuss complex ion formation in terms of the electronic configurations of the simple substances involved.
12. Explain the fact that cupric ions do not yield a precipitate of the hydroxide in the presence of an excess of ammonia.
13. What are hydroxide complex ions? Why does zinc hydroxide dissolve in an excess of sodium hydroxide while manganous hydroxide does not?
14. Explain complex ion formation in terms of ionic equilibria.
15. How can it be shown that the cyanide complex ions of copper and cadmium are more stable than the ammonia complex ions?

SUPPLEMENTARY READINGS

Hammett, L. P., *Solutions of Electrolytes*, McGraw-Hill Book Company, Inc., New York, 1936.

Hogness, T. R., and W. C. Johnson, *Qualitative Analysis and Chemical Equilibrium*, Henry Holt and Company, Inc., New York, 1937.

Kelsey, E. B., and H. G. Dietrich, *Fundamentals of Semimicro Qualitative Analysis*, The Macmillan Company, New York, 1940.

Chapter 19

OXIDATION–REDUCTION IN SOLUTION.
OXYCOMPOUNDS OF THE HALOGENS.
HYDROGEN PEROXIDE

Oxidation-reduction is a chemical reaction in which the oxidation number of one element or radical is increased, while that of another is correspondingly decreased. Oxidation numbers in electrovalent compounds are equal to the electronic differences between the ions and the atoms in uncombined state. Consequently, oxidation-reduction involving ionic substances is a reaction in which a transfer of electrons occurs, and *oxidation is the loss of electrons while reduction is the gain of electrons.* In oxidation-reduction between compound ions, the electron change is not attributed to a particular atom in the ion, but to the reaction affecting the whole ion. This usually requires interaction with some additional substance, such as hydrogen ions, hydroxide ions, or water molecules.

Oxidizing Agents. Substances causing the oxidation of other substances are oxidizing agents. Therefore, they must contain atoms or ions capable of gaining or sharing additional electrons, so as to cause an increase in the oxidation number of the atoms from which the electrons are taken. *Metal ions and hydronium ions* are oxidizing agents because they may gain electrons to neutralize their electric charges. *Elementary nonmetals* which form simple negative ions gain electrons in the process so that they also are oxidizing agents. *The oxyacids and oxyanions* of a number of the nonmetals, such as the halogens, nitrogen, and sulfur, are oxidizing agents under proper experimental conditions. The oxidizing action of these substances usually, but not always, involves interaction with hydrogen ions. Specific reactions to illustrate the behavior of these types of oxidizing agents are discussed in the subsequent paragraphs.

Reducing Agents. Substances causing the reduction of other substances are reducing agents. They must be capable of releasing

electrons. *The elementary metals* give up electrons in the formation of their positive ions. *Metal ions having low electrovalence* are reducing agents when the metal is capable of forming ions in more than one state of oxidation. *Simple negative ions,* such as chloride, bromide, iodide, and sulfide ions, release electrons in reactions that oxidize them to elementary nonmetals. Many of the *nonmetals* may be oxidized to form molecules and anions in which they have positive oxidation numbers. Usually, these reactions involve interaction with water molecules or with hydroxide ions releasing electrons in the process. Molecules and anions, containing *a nonmetallic element in an intermediate positive state of oxidation,* serve as reducing agents in the reactions by which they are changed to higher states of oxidation, as for example, in the conversion of sulfites into sulfates.

Oxidation-Reduction Potentials. The materials involved in ionic oxidation-reduction may be arranged in two half cells. (See page 236.) In the displacement of cadmium ions by zinc, for example, one half cell consists of the zinc electrode in a solution containing zinc ions in such concentration that the activity is 1.

$$Zn \rightleftharpoons Zn^{++} + 2\,\epsilon$$

The other half cell is a similar arrangement of cadmium and a solution of a cadmium salt.

$$Cd \rightleftharpoons Cd^{++} + 2\,\epsilon$$

The electrode potential of each of these half cells toward the standard reference electrode, the hydrogen electrode, may be measured experimentally. This electrode potential is called the *standard oxidation-reduction potential.* It is a measure of the activity of the particular substance in oxidation-reduction. The difference in potential of each individual half cell toward the standard half cell depends on the activity of the reactants. Under definite concentration and temperature conditions, a specific oxidation-reduction potential is characteristic of each oxidizing agent and of each reducing agent. Complete cells are made by connecting the different half cells through the use of ionic solutions and metallic conductors. Different oxidizing agents may be used with the same reducing agent, and different reducing agents with the same oxidizing agent. Just as

the complete cell requires the assembling of the two half cells, so the complete equation demands the combination of the two partial equations.

Oxidation-Reduction in Acidic Solution. Oxidation by oxy-compounds is usually carried out in acidic solution, because protons in addition to electrons enter into most of these changes. Hence, the activity of the oxidizing agent is increased by the presence of hydronium ions, although acid molecules and water molecules may also serve as proton donors. To illustrate the development of equations representing this type of oxidation-reduction, a weak acid, a strong acid, and a salt are selected as oxidizing agents. The same reducing agent, zinc, may be used with each of these oxidizing agents.

Two ion-electron partial equations are written as in oxidation-reduction involving simple substances. Each of the partial equations represents a half reaction and must be balanced with respect to both the numbers of atoms and the electric charges. In the equations representing oxidation-reduction reactions, the protons that are taken up or split off may be represented by the symbol H^+, in preference to H_3O^+.

Oxidation in weakly acidic solution may be illustrated by the reaction of zinc with hypochlorous acid. Although zinc may displace hydrogen from a number of acids, hydrogen is not produced in this reaction, because the oxidizing action of hypochlorous acid is greater than that of hydronium ions alone. The equations for the half reactions are derived according to definite rules. As in all chemical reactions it is necessary to know the composition of the products formed. The reduction of hypochlorous acid by active reducing agents produces chloride ions. Since hypochlorous acid is a weak electrolyte, it is represented by the molecular formula. The formula of the oxidizing agent and the symbols for hydrogen ion and electron are written to the left and of chloride ions and water to the right of the reaction symbol.

$$HClO + H^+ + \epsilon \longrightarrow Cl^- + H_2O$$
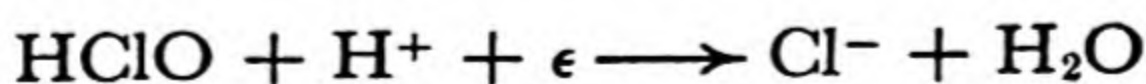
The partial equation, as written above, is balanced with respect to atoms, but is not balanced in terms of electric charges. An excess of one unit of positive charge is shown by the ions to the left of the

reaction symbol and an excess of one unit of negative charge to the right. Hence, two electrons are required to balance the equation with respect to electric charge.

$$HClO + H^+ + 2\,\epsilon \longrightarrow Cl^- + H_2O$$
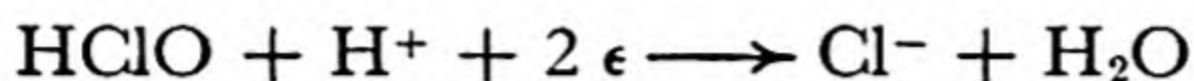
This partial equation means that hypochlorites are reduced in acidic solution by any substance that furnishes electrons with sufficiently great activity. The standard oxidation-reduction potential for this reaction is $+ 1.63$ volts at $25°$. Hence, hypochlorous acid is an active oxidizing agent. The oxidation of zinc is shown by the partial equation:

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon$$
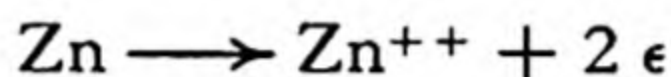
The equation for the oxidation of zinc by hypochlorites in acidic solution is the sum of the two partial equations.

$$HClO + H^+ + Zn \longrightarrow Cl^- + Zn^{++} + H_2O$$
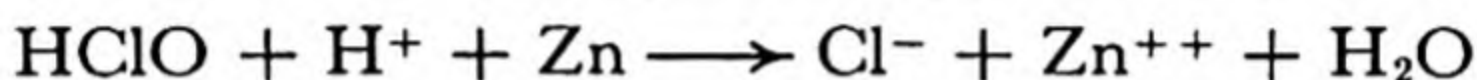
The oxidation of zinc by nitric acid is similar to the reaction with hypochlorous acid, except that nitric acid is a strong acid represented by ionic rather than molecular formula. The principal reduction product of nitric acid in moderately concentrated solution, approximately 6 M., is nitric oxide, NO. Therefore, the incomplete expression for the half reaction is:

$$NO_3^- + H^+ + \epsilon \longrightarrow NO + H_2O$$
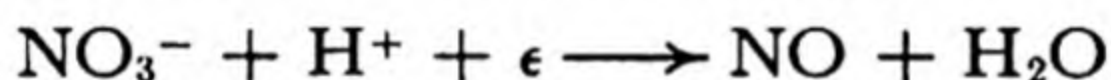
Obviously this is not balanced, because the two oxygen atoms removed from the nitrate ion require four hydrogen ions and produce two molecules of water.

$$NO_3^- + 4\,H^+ + \epsilon \longrightarrow NO + 2\,H_2O$$
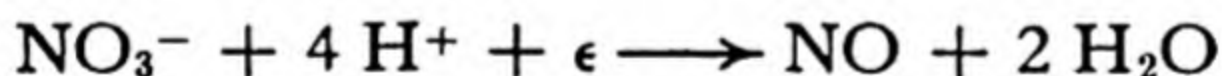
The products of this half reaction are neutral molecules. Hence, the net charge of the initial substances is also zero, and three electrons must be gained in the reduction of the nitrate ion to form nitric oxide.

$$NO_3^- + 4\,H^+ + 3\,\epsilon \longrightarrow NO + 2\,H_2O$$

Zinc is the source of the electrons for this reduction.

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon$$

Each nitrate ion reduced requires three electrons and each zinc atom oxidized supplies two. Hence, six is the unit number of elec-

trons that gives the correct ratio. The partial equations are multiplied by two and three, respectively, and then added with the cancellation of the electron symbols.

$$[NO_3^- + 4\,H^+ + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 2$$
$$[Zn \longrightarrow Zn^{++} + 2\,\epsilon] \times 3$$
$$\overline{2\,NO_3^- + 8\,H^+ + 3\,Zn \longrightarrow 2\,NO + 3\,Zn^{++} + 4\,H_2O}$$
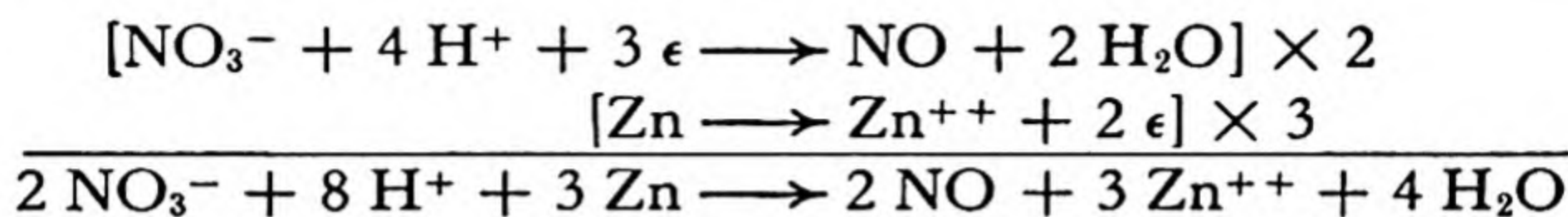
The oxidation of zinc by an acidic solution of potassium permanganate may now be derived directly by filling in the appropriate numbers in the partial equations, without rewriting as in the preceding examples. Potassium ions from the salt do not enter into the reaction. The permanganate ion, MnO_4^-, is reduced in acidic solution to form the manganous ion, Mn^{++}.

$$[MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O] \times 2$$
$$[Zn \longrightarrow Zn^{++} + 2\,\epsilon] \times 5$$
$$\overline{2\,MnO_4^- + 16\,H^+ + 5\,Zn \longrightarrow 2\,Mn^{++} + 5\,Zn^{++} + 8\,H_2O}$$
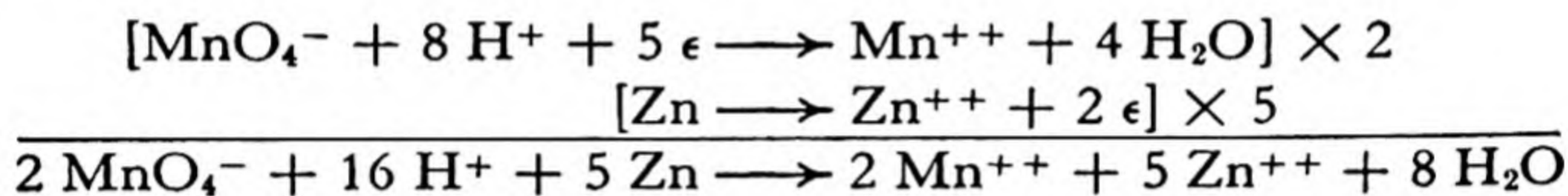
Oxidation Products in Acidic Solution. The composition of the product formed by the oxidation of a specific substance depends on the nature of the substance. For each of the classes of reducing agents, listed in a preceding paragraph, a general statement may be made concerning the type of product formed by its oxidation in acidic solution. To emphasize the nature of the product of oxidation, the same oxidizing agent will be used in the examples which follow. The electronic changes for the substances in three of these classes involve simple processes, *i.e.*, the electronic change does not require interaction of the reducing agent with molecules or ions of the solvent. *Metals are oxidized in acidic solution to form positive ions.* The equations expressing the behavior of zinc are examples of this type. *Metal ions in a low state of oxidation may be oxidized to higher states of oxidation*, if such ions exist. Ferrous ions are oxidized to the ferric state by hypochlorous acid.

$$[HClO + H^+ + 2\,\epsilon \longrightarrow Cl^- + H_2O] \times 1$$
$$[Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon] \times 2$$
$$\overline{HClO + H^+ + 2\,Fe^{++} \longrightarrow Cl^- + 2\,Fe^{+++} + H_2O}$$
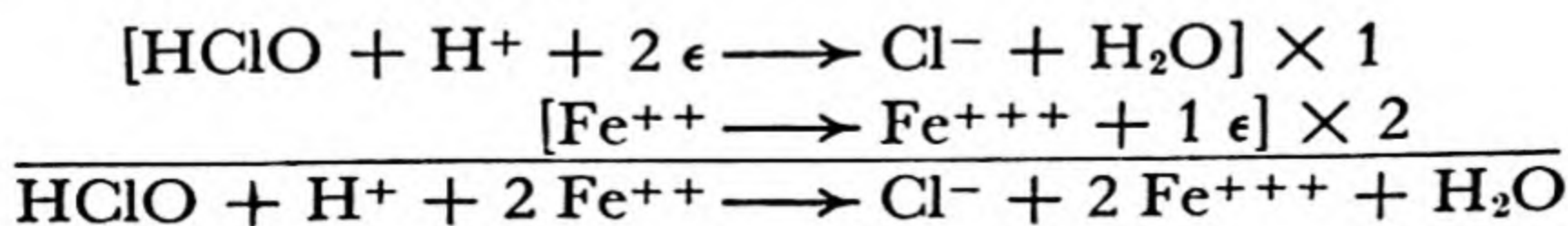
Simple negative ions are oxidized to form the free nonmetal as the first product. An excess of a strong oxidizing agent may cause the further

oxidation of the free nonmetal. Iodides are oxidized by hypochlorous acid to form free iodine, which is further oxidized by an excess of hypochlorous acid.

$$HClO + H^+ + 2\,\epsilon \longrightarrow Cl^- + H_2O$$
$$2\,I^- \longrightarrow I_2 + 2\,\epsilon$$
$$\overline{HClO + H^+ + 2\,I^- \longrightarrow Cl^- + I_2 + H_2O}$$
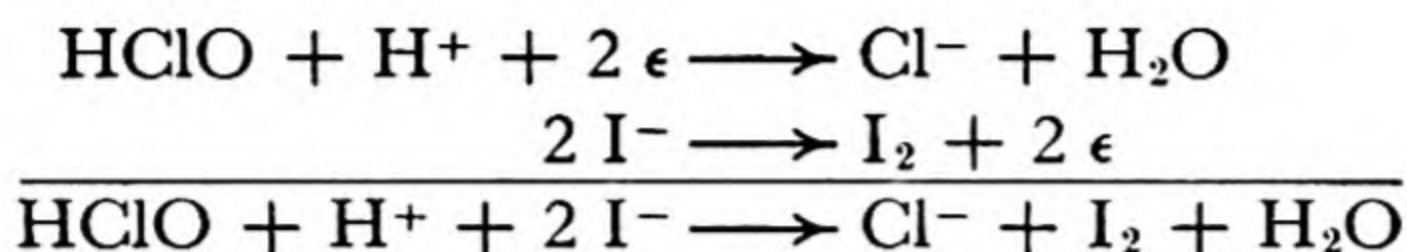
The oxidation of the two remaining classes of common reducing agents is somewhat more complex. *Elementary nonmetals are oxidized in acidic solution to yield oxyanions* containing the nonmetals in their higher states of oxidation. If these anions yield weak acids, molecular acid instead of the anion is the product, and a nonmetal oxide is produced if the acid is unstable under experimental conditions. The formation of the oxyanion involves the interaction of nonmetal atoms with water as the source of oxygen, and hydrogen ions are formed. The rules for deriving the partial equation for the half reaction showing the oxidation of the nonmetal in acidic solution are: *first*, to learn what the products of the reaction are; *second*, to represent the nonmetal and the water to the left of the reaction symbol and the oxyanion or molecule and hydrogen ions to the right; *third*, to balance the partial equation by showing equal numbers of each variety of atom on both sides of the reaction symbol; *fourth*, to balance the charges by adding the correct number of electrons. The completed partial equation is now brought into electronic agreement with the partial equation showing the reduction of the oxidizing agent. The oxidation of elementary iodine by hypochlorous acid illustrates these steps. The product of the oxidation of iodine is iodic acid, a strong acid that may be represented by the symbols, H^+ and IO_3^-. The reduction of the hypochlorous acid is represented by the partial equation written in preceding paragraphs.

$$HClO + H^+ + 2\,\epsilon \longrightarrow Cl^- + H_2O$$
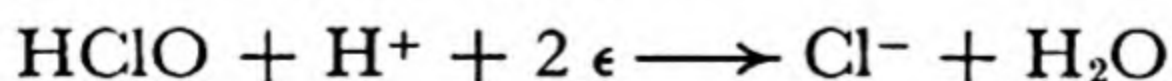
According to the rules listed above, the other partial equation is derived by a succession of operations.

$$I_2 + H_2O \longrightarrow IO_3^- + H^+$$
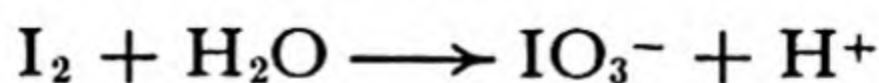
Two atoms of iodine produce $2\,IO_3^-$, requiring six atoms of oxygen from $6\,H_2O$, and $12\,H^+$ ions are released.

$$I_2 + 6 H_2O \longrightarrow 2 IO_3^- + 12 H^+$$
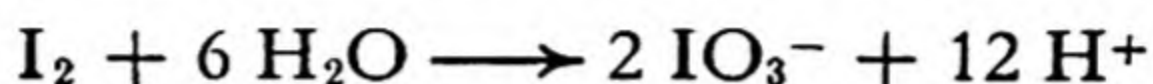
Ten electrons must be represented to the right to balance the charges. The unit change of the oxidizing agent is two electrons. Hence, the half reaction for its reduction is multiplied by five in order to bring the two partial equations into agreement. The completed equation for the behavior of the reducing agent is written, and the two partial equations are added with the cancellation of materials represented on both sides of the reaction symbol.

$$5 HClO + 5 H^+ + 10 \epsilon \longrightarrow 5 Cl^- + 5 H_2O$$
$$I_2 + 6 H_2O \longrightarrow 2 IO_3^- + 12 H^+ + 10 \epsilon$$
$$\overline{5 HClO + H_2O + I_2 \longrightarrow 5 Cl^- + 2 IO_3^- + 7 H^+}$$
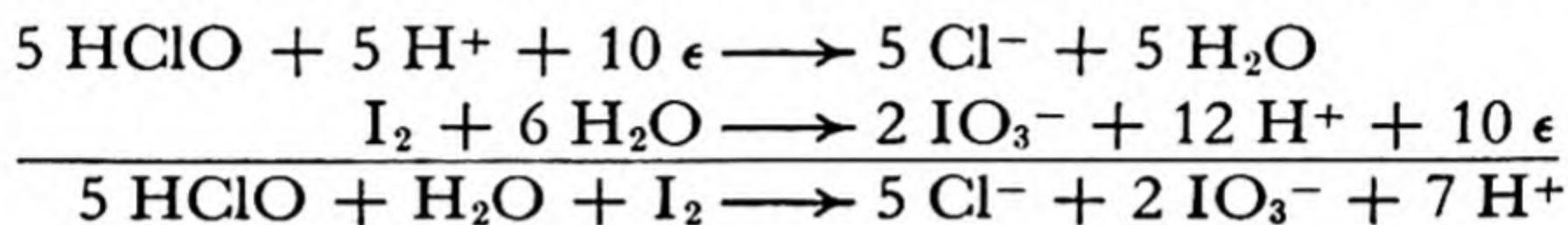
Although the procedure seems complicated, each step follows logically from the preceding step.

Oxyanions and oxyacid molecules containing nonmetals in lower states of oxidation are oxidized to produce oxyradicals of the elements in high states of oxidation. The principles are the same as in the oxidation of the elementary nonmetals. Sulfurous acid, H_2SO_3, a weak acid, is oxidized by hypochlorous acid to form sulfuric acid, H_2SO_4, a strong acid. Water is represented as the source of the additional atom of oxygen in the partial equation, with sulfate ions and hydrogen ions as the products.

$$HClO + H^+ + 2 \epsilon \longrightarrow Cl^- + H_2O$$
$$H_2SO_3 + H_2O \longrightarrow SO_4^{--} + 4 H^+ + 2 \epsilon$$
$$\overline{HClO + H_2SO_3 \longrightarrow Cl^- + SO_4^{--} + 3 H^+}$$
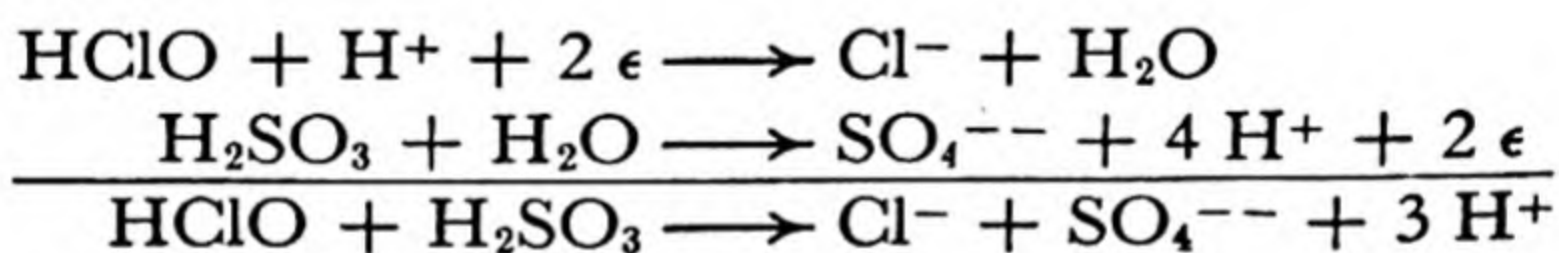
Oxidation in Basic Solution. The stability of the oxyanions is much greater in basic than in acidic solution. Consequently, the oxidizing activity is much less, and some oxyanions do not exhibit active oxidizing action in basic solution, *e.g.*, nitrate and sulfate ions. Other anions, such as hypochlorite, are active oxidizing agents even in basic solutions. Water molecules are the source of the hydrogen ions required in the half reaction representing the decomposition of the oxidizing agent under these conditions. The half reaction for the reduction of hypochlorite ions in basic solution is:

$$ClO^- + H_2O + 2 \epsilon \longrightarrow Cl^- + 2 OH^-$$
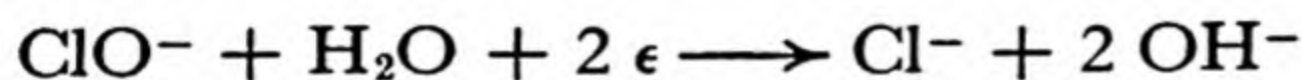
The activity of a nonmetallic reducing agent is increased by the greater stability of the oxyanions formed in basic solution. Hy-

droxide ions are represented as the source of oxygen atoms in the partial equations. The change is opposite in nature to that shown by the half reaction for the behavior of the oxidizing agent.

$$SO_3^{--} + 2\,OH^- \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon$$
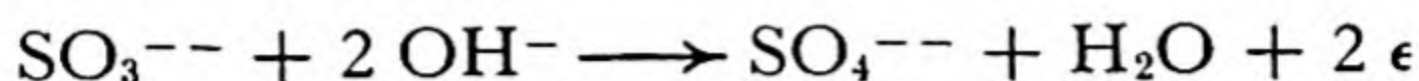
In the addition of these two partial equations, water molecules and hydroxide ions in addition to electrons cancel.

$$ClO^- + SO_3^{--} \longrightarrow Cl^- + SO_4^{--}$$

This means that the same number of hydroxide ions are produced as are used up in this reaction.

Sodium peroxide, Na_2O_2, is frequently used as an oxidizing agent in basic solutions. The metachromite ion, $Cr(OH)_4^-$, is oxidized to the chromate, CrO_4^{--}, by sodium peroxide.

$$[Na_2O_2 + 2\,H_2O + 2\,\epsilon \longrightarrow 2\,Na^+ + 4\,OH^-] \times 3$$
$$\underline{[Cr(OH)_4^- + 4\,OH^- \longrightarrow CrO_4^{--} + 4\,H_2O + 3\,\epsilon] \times 2}$$
$$3\,Na_2O_2 + 2\,Cr(OH)_4^- \longrightarrow 6\,Na^+ + 2\,CrO_4^{--} + 4\,OH^- + 2\,H_2O$$
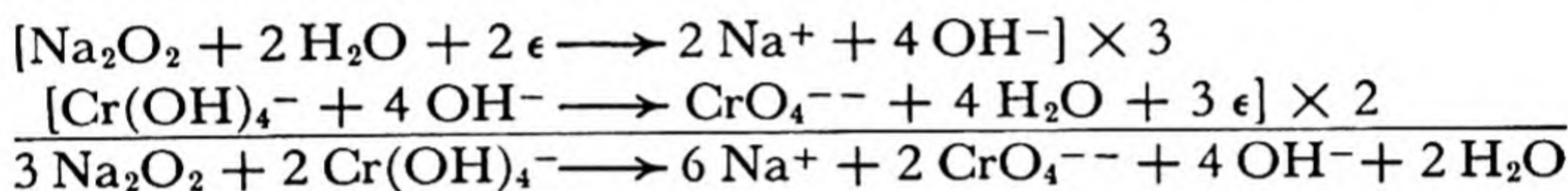
Ferrous hydroxide in suspension in water is slowly oxidized by oxygen absorbed from air, with the formation of ferric hydroxide.

$$O_2 + 2\,H_2O + 4\,\epsilon \longrightarrow 4\,OH^-$$
$$\underline{[Fe(OH)_2 + OH^- \longrightarrow Fe(OH)_3 + \epsilon] \times 4}$$
$$O_2 + 4\,Fe(OH)_2 + 2\,H_2O \longrightarrow 4\,Fe(OH)_3$$
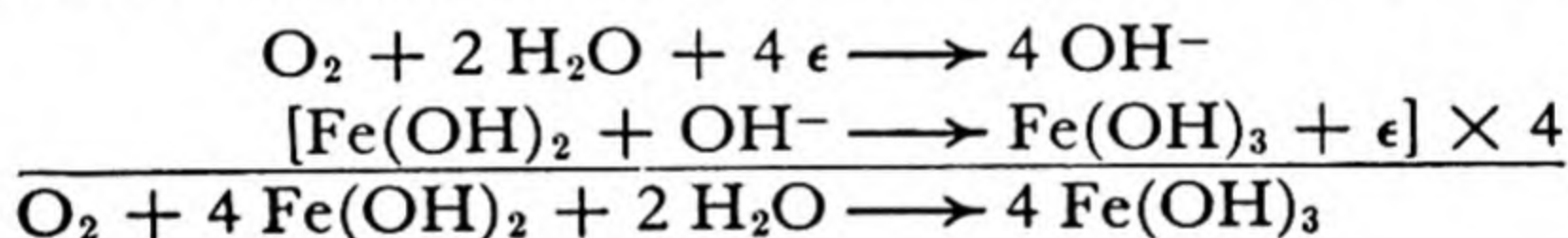
OXYCOMPOUNDS OF THE HALOGENS

Although the halogens do not combine directly with oxygen, a number of oxycompounds of the halogens are known. The oxides of bromine and some of the oxides of chlorine and iodine are unstable, decomposing rapidly at ordinary temperatures. *The oxide of fluorine*, F_2O, may be prepared by the reaction of fluorine with a dilute solution of sodium hydroxide. In the absence of reducing agents, it is a stable gas at room temperature, but it is an active oxidizing agent. The most important oxides of chlorine are the *monoxide*, Cl_2O, the *dioxide*, ClO_2, and the *heptoxide*, Cl_2O_7; of iodine, the *tetroxide*, I_2O_4, and the *pentoxide*, I_2O_5. These oxides may be produced by the decomposition of the various oxyacids. Each of the halogens, except fluorine, yields oxyacids and oxysalts. The oxyacids are listed in Table 27.

TABLE 27. OXYACIDS OF THE HALOGENS

Oxidation Number	Name	Chlorine	Bromine	Iodine
1 +	Hypohalous	$HClO$	$HBrO$	HIO
3 +	Halous	$HClO_2$	—	—
5 +	Halic	$HClO_3$	$HBrO_3$	HIO_3
7 +	Perhalic	$HClO_4$	—	HIO_4

The halogens exhibit positive oxidation numbers in these compounds. The acids have varying degrees of stability toward heat and are affected also by changes in concentration. They are usually liberated from their salts as desired for reaction, in preference to storing them for future use. Many of these oxycompounds decompose with explosive violence. In each of these classes of substances, the chlorine compounds are the most important.

Hypochlorites. Hypochlorous Acid. Chlorine reacts with water, producing low concentrations of hydrochloric acid and hypochlorous acid in equilibrium with dissolved chlorine. Hypochlorous acid is a weak electrolyte.

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO$$
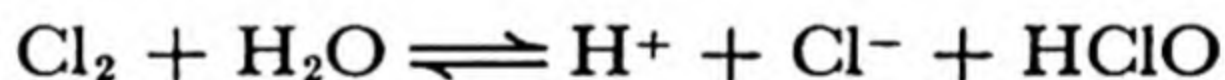
The acids are neutralized in the presence of a base, and the reaction approaches completion, producing a mixture of chloride and hypochlorite.

$$Cl_2 + 2\,OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

Solutions of sodium hypochlorite are prepared commercially by passing chlorine into cold solutions of sodium hydroxide, and by electrolysis of sodium chloride solutions with both electrodes in a single compartment cell. Chlorine, liberated at the anode, reacts with the basic solution formed about the cathode. Chlorine reacts with calcium hydroxide to form a mixed salt with the two negative ions, chloride and hypochlorite, in combination with the same positive ion. This mixed salt is known as *bleaching powder* and also as *chloride of lime*. It is prepared industrially by passing chlorine over solid calcium hydroxide spread on trays in a large reaction chamber.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaCl(ClO) + H_2O$$
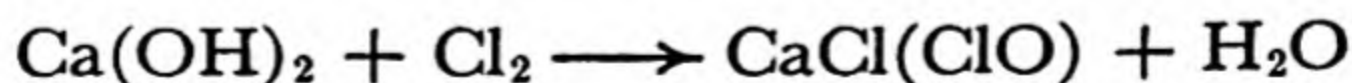
Hypochlorites decompose in contact with cobalt hydroxide as a catalyst, with the evolution of oxygen.

$$2\,ClO^- \longrightarrow 2\,Cl^- + O_2$$
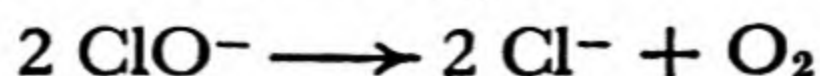
A mixture of chloride and chlorate is produced by heating a solution of an hypochlorite. A compensating oxidation-reduction, called *auto-oxidation-reduction*, occurs in this reaction. The same substance serves as both the oxidizing and the reducing agent. This is due to the fact that a mixture of chlorine compounds in the oxidation states $1-$ and $5+$ is more stable than the single compound containing the element in the $1+$ state of oxidation.

$$[ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-] \times 2$$
$$ClO^- + 4\,OH^- \longrightarrow ClO_3^- + 2\,H_2O + 4\,\epsilon$$
$$\overline{3\,ClO^- \longrightarrow 2Cl^- + ClO_3^-}$$
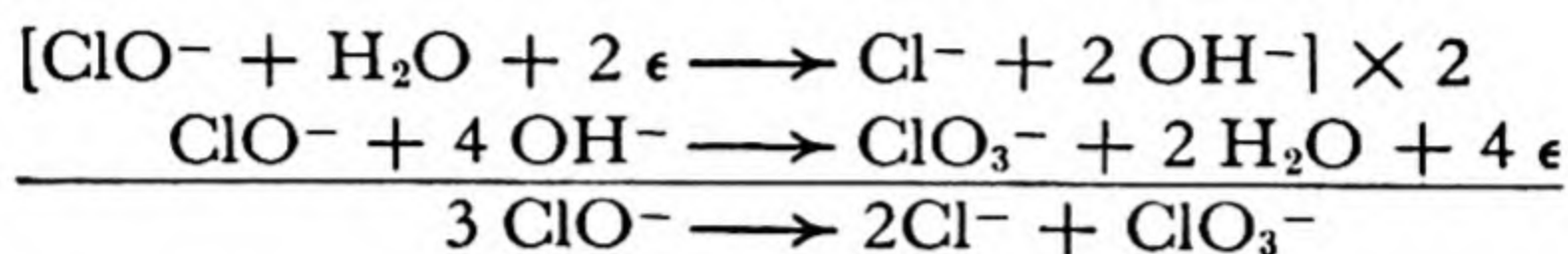
Hypochlorites react with acids, producing hypochlorous acid. If a mixture of chloride and hypochlorite is acidified with a strong acid, the concentration of hypochlorous acid in the solution is so great that it reacts with chloride ions to form free chlorine.

$$ClO^- + H^+ \rightleftharpoons HClO$$
$$HClO + Cl^- + H^+ \rightleftharpoons H_2O + Cl_2$$
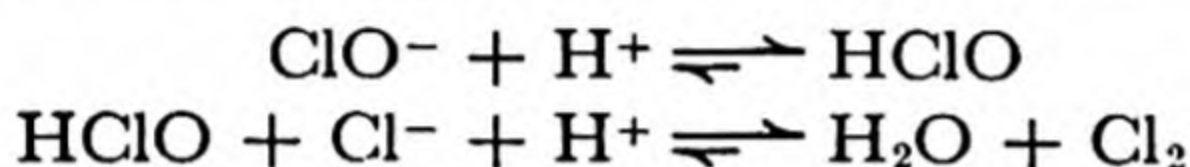
The concentration of hypochlorous acid in weakly acidic solutions is so low that the loss of chlorine takes place only slowly. The concentration of hypochlorous acid is regulated by controlling the concentration of hydrogen ions and, in this manner, it is possible to maintain the concentration of molecular hypochlorous acid at a constant value until all of the salt is decomposed. Solutions of this type, known as *Dakin's solution*, are used for the irrigation of infected wounds.

The hypochlorites are important as bleaching, deodorizing, and disinfecting agents. The chloride and hypochlorite mixture produced directly is suitable for these uses. Most of these uses depend on the properties of hypochlorous acid; and liquid chlorine, stored and transported in strong steel cylinders, is now used in preference to the hypochlorites for many purposes.

Hypochlorous acid is unstable in sunlight, decomposing to give off oxygen.

$$2\,HClO \longrightarrow 2\,H^+ + 2\,Cl^- + O_2 \uparrow$$
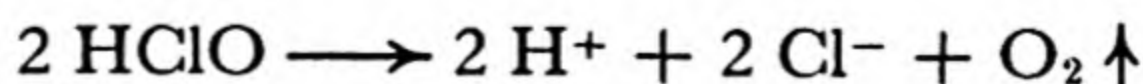
Chlorine monoxide may be prepared by the reaction of chlorine with mercuric oxide at a temperature of about 0°.

$$2\,HgO + 2\,Cl_2 \longrightarrow HgCl_2HgO + Cl_2O$$
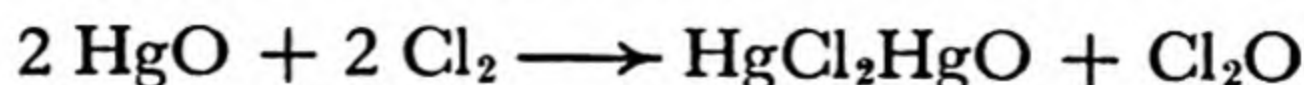
Chlorine monoxide is an unstable, yellowish-brown gas at room temperature. It reacts reversibly with water to form hypochlorous acid.

$$Cl_2O + H_2O \rightleftharpoons 2\ HClO$$
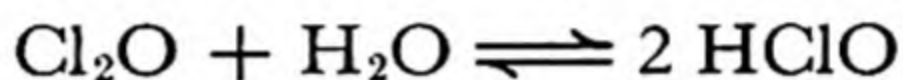
Hypobromites and Hypoiodites. Bromine and iodine react with water to a smaller degree than chlorine, but they react with cold, strongly basic solutions to form hypobromites and hypoiodites, respectively. These salts are converted also into the corresponding halide and halate when their solutions are warmed. The reaction of bromine with mercuric oxide produces bromine monoxide. This oxide is very unstable and is not important.

Chlorates. Chloric Acid. Potassium chlorate, $KClO_3$, the most important of the chlorates, is prepared commercially by electrolysis of hot saturated solutions of potassium chloride in a simple cell. The solution is stirred to insure mixing of the chlorine and the hydroxide formed as direct products of electrolysis. The chlorate is formed because the hypochlorite is not stable in hot solution. Potassium chlorate has only moderate solubility so that it crystallizes from the solution. Sodium chlorate may be prepared in a similar manner, except that it is much more soluble in water, and the production of the pure solid requires additional separations. The decomposition of potassium chlorate in contact with manganese dioxide at about 200° is the common laboratory reaction for the preparation of oxygen. When the solid is heated for some time at a temperature just above its melting point, 368°, approximately one fifth of a sample decomposes to form chloride and oxygen, while the remainder is converted into a mixture of chloride and perchlorate.

$$4\ KClO_3 \longrightarrow 3\ KClO_4 + KCl$$
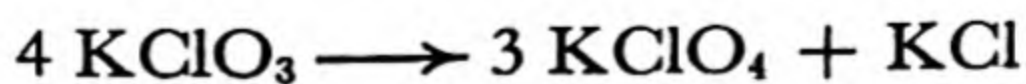
The chlorates are active oxidizing agents but are more stable toward reduction than the hypochlorites. Potassium chlorate is used in some types of pyrotechnic mixtures for airplane flares and as an oxidizing agent in primer caps. It is also used in incendiary projectiles.

A solution of chloric acid may be prepared by the reaction of sulfuric acid with a solution of barium chlorate. Barium sulfate is precipitated, leaving the ions of the acid in solution. Chloric acid

is unstable in concentrated solution at temperatures above 40°. It may decompose to form hydrochloric acid and oxygen, hydrochloric acid and perchloric acid, or chlorine dioxide, water, and oxygen.

$$4\ HClO_3 \longrightarrow 2\ H_2O + 4\ ClO_2 + O_2$$
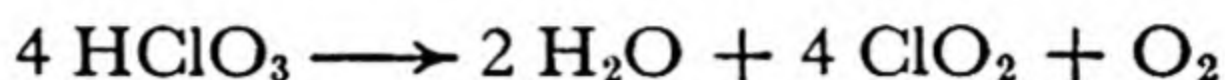
Chlorine dioxide is a yellow gas which decomposes with explosive violence. Consequently, the addition of concentrated sulfuric acid to a solid chlorate may cause a dangerous explosion.

Chlorites. Chlorous Acid. Chlorine dioxide reacts with basic hydroxides to form a mixture of chlorite and chlorate.

$$2\ ClO_2 + 2\ OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$
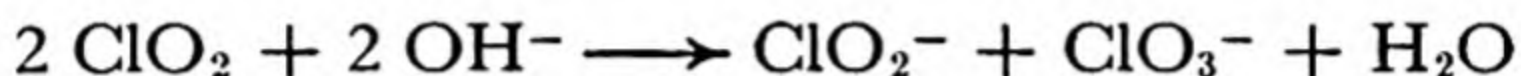
Chlorous acid is prepared from its salts by reaction with stronger acids. Both chlorous acid and its salts are unstable toward heat, decomposing to form either the chloride and oxygen or the chloride and chlorate. Sodium chlorite is prepared in commercial quantities for use as a bleaching agent. It is active enough to oxidize the natural coloring matter in cotton, wood pulp, and other cellulose fibers, without materially damaging the fiber. The chlorites act as bleaching agents in both acidic and basic solutions.

Perchlorates. Perchloric Acid. The formation of perchlorates by the decomposition of chlorates has been mentioned in the discussion of the chlorates. Potassium perchlorate is much less soluble than the chloride and, consequently, separation may be made by fractional crystallization. Sodium perchlorate is made industrially by electrolysis of concentrated solutions of sodium chlorate, using platinum anodes and iron cathodes. The chlorate is oxidized to the perchlorate at the anode, and hydrogen is discharged at the cathode. Potassium and ammonium perchlorates are prepared from sodium perchlorate by precipitation, since they have lower solubilities. Potassium perchlorate is used in primer mixtures and to supply oxygen in magnesium and aluminum flares.

Oxidizing Activity of the Oxycompounds of Chlorine. The electrovalent negative ion shows the most stable oxidation state of chlorine. Compounds containing the element in other stages of oxidation are unstable toward reduction, but the stability increases from oxidation number 1 + to 7 +. This is demonstrated by spontaneous changes in oxidation numbers when the compounds are

heated. Consequently, these oxycompounds are oxidizing agents of varying degrees of activity, and the hypochlorites are more active oxidizing agents than the chlorates or the perchlorates. The reduction of the chlorate or the perchlorate yields the chloride, not the lower oxysalt.

HYDROGEN PEROXIDE

Hydrogen peroxide contains twice as much oxygen for the same weight of hydrogen as the simple oxide, water. Its formula is H_2O_2, and it contains the peroxide radical composed of two atoms of oxygen bound by shared electrons. The valence of the radical is 2 —. Hydrogen peroxide is a weak acid, containing two replaceable atoms of hydrogen. There are a number of peroxy compounds, hydrogen peroxide being the simplest. The oxyacids are structurally hydroxides of nonmetals. The peroxy compounds contain the peroxide group, —OOH, in place of the hydroxide group, —OH. Thus, water is H—OH and hydrogen peroxide, H—OOH. The formula of metaboric acid, HBO_2, may be written H—O—B$=$O, and of peroxyboric acid, H—O—O—B$=$O. Peroxydisulfuric acid, $H_2S_2O_8$, is one of the more important of these compounds. All of the peroxyacids exhibit oxidizing action. The peroxide radical, like the hypochlorite radical, is composed of two nonmetal atoms with an unstable electron bond, which contributes oxidizing properties in both basic and acidic solutions.

Peroxides of Metals. Peroxides are binary compounds containing larger proportions of oxygen than the simple oxide. Sodium burns in air with the formation of peroxide at temperatures above 300°.

$$2\,Na + O_2 \longrightarrow Na_2O_2$$
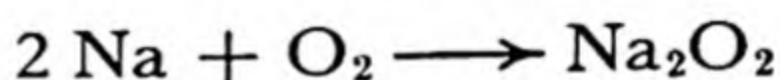
Barium peroxide is formed by the reaction of barium oxide with oxygen of the air at a pressure of one atmosphere and a temperature of 500°.

$$2\,BaO + O_2 \longrightarrow 2\,BaO_2$$
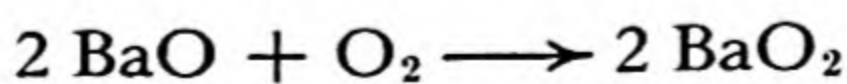
Peroxides differ in structure from the ordinary dioxides. In terms of atomic structures, an electron pair constitutes a bond between the two oxygen atoms in the peroxide radical, but the two oxygen

atoms in a dioxide are not bonded in this manner. Barium in barium peroxide has an oxidation number of 2 +, but lead in lead dioxide, PbO_2, has an oxidation number of 4 +.

Preparation of Hydrogen Peroxide. Hydrogen peroxide may be prepared by the action of an acid on a metal peroxide. Usually, barium peroxide and sulfuric acid are employed for this. Barium sulfate is very slightly soluble so that it is easily separated by filtration.

$$BaO_2 + 2\,H^+ + SO_4^{--} \longrightarrow BaSO_4 \downarrow + H_2O_2$$
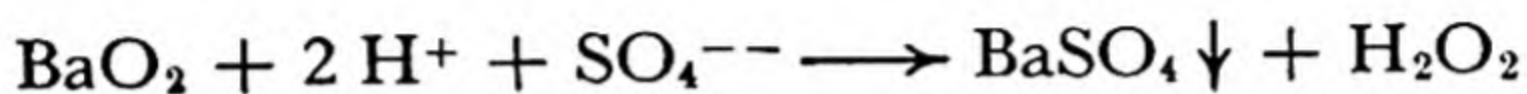
Soluble barium salts are poisonous, so that their presence in hydrogen peroxide would be objectionable for use in germicidal and antiseptic solutions.

Hydrogen peroxide is also prepared by electrolysis of sulfuric acid of specific gravity, 1.35–1.45. The principal product at the anode, when high electrical potential is applied, is peroxydisulfuric acid, $H_2S_2O_8$, instead of oxygen, the usual anode product of the electrolysis of sulfuric acid solutions. The partial equation for this half reaction is:

$$2\,HSO_4^- \longrightarrow H_2S_2O_8 + 2\,\epsilon$$
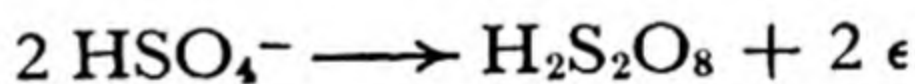
Hydrogen is discharged at the cathode. Peroxydisulfuric acid hydrolyzes in two stages, first forming peroxymonosulfuric acid, known also as *Caro's acid*, H_2SO_5.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$
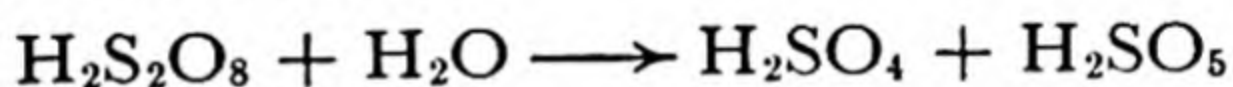
This latter compound hydrolyzes to produce sulfuric acid and hydrogen peroxide.

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$
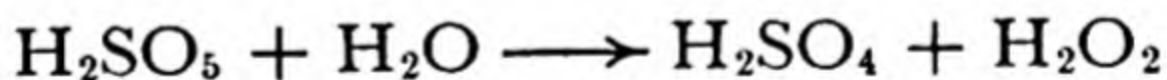
Properties and Reactions of Hydrogen Peroxide. Hydrogen peroxide has a lower vapor pressure than water. Hence, it may be concentrated by evaporation, usually under reduced pressure to permit the use of lower temperatures and thus minimize decomposition. The pure substance is a syrupy liquid that freezes at $-\,2°$. The molecules of this liquid have high polarity, and, consequently, hydrogen peroxide is an even better ionizing solvent than water. Hydrogen peroxide decomposes with explosive violence if the pure liquid or a concentrated solution is heated. Dilute solutions are stable if kept in a dark and cool place. Decomposition is retarded

by acetanilide and accelerated by pulverized metals, manganese dioxide, saliva, blood serum, and many other materials. The ordinary pharmaceutical solution contains approximately 3 per cent of hydrogen peroxide.

The decomposition of hydrogen peroxide is a highly exothermic reaction.

$$2 H_2O_2 \longrightarrow 2 H_2O + O_2 + 46,200 \text{ cal.}$$
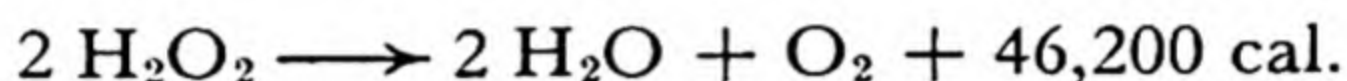
Since hydrogen peroxide is an oxidizing agent, which may supply oxygen directly, it is used as a bleaching agent. It is suitable for bleaching hair, silk, feathers, and certain other materials that may be damaged by the more energetic action of hypochlorous acid. The most familiar use of hydrogen peroxide is as a germicidal and antiseptic solution.

Hydrogen peroxide is an oxidizing agent of sufficient activity to liberate iodine in acidic or basic solution. In acidic solution the reaction is:

$$H_2O_2 + 2 H^+ + 2 \epsilon \longrightarrow 2 H_2O$$
$$\underline{2 I^- \longrightarrow I_2 + 2 \epsilon}$$
$$H_2O_2 + 2 H^+ + 2 I^- \longrightarrow 2 H_2O + I_2$$

In basic solution:

$$H_2O_2 + 2 \epsilon \longrightarrow 2 OH^-$$
$$\underline{2 I^- \longrightarrow I_2 + 2 \epsilon}$$
$$H_2O_2 + 2 I^- \longrightarrow 2 OH^- + I_2$$
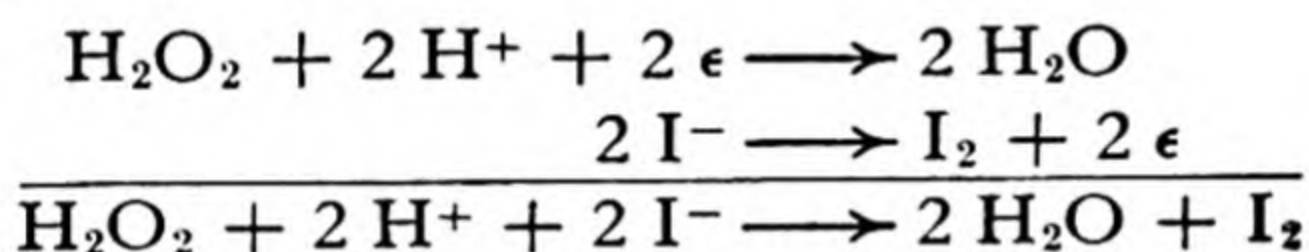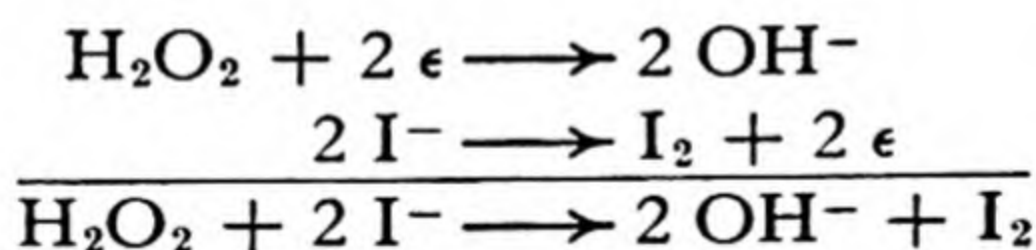
The peroxide radical may be oxidized by strong oxidizing agents. Hydrogen peroxide reduces acidic solutions of potassium permanganate, with the formation of oxygen and a manganous salt.

$$[MnO_4^- + 8 H^+ + 5 \epsilon \longrightarrow Mn^{++} + 4 H_2O] \times 2$$
$$\underline{[H_2O_2 \longrightarrow 2 H^+ + O_2 + 2 \epsilon] \times 5}$$
$$2 MnO_4^- + 6 H^+ + 5 H_2O_2 \longrightarrow 2 Mn^{++} + 5 O_2 + 8 H_2O$$
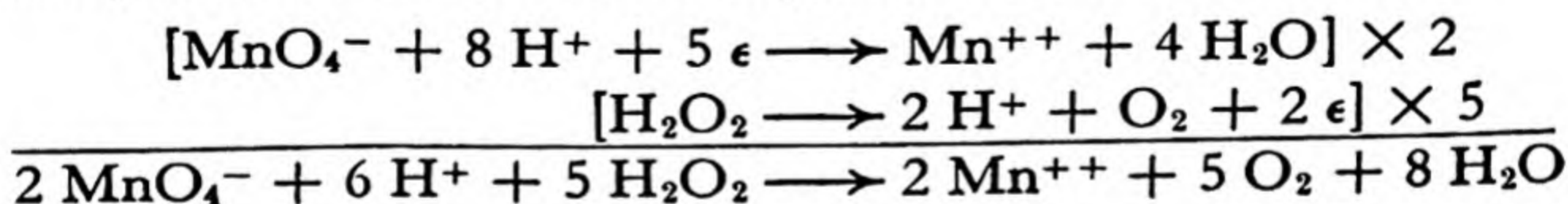
EXERCISES

1. What is meant by oxidation-reduction?
2. What are oxidizing agents? reducing agents? Into what groups may oxidizing and reducing agents be conveniently classified?
3. How can the electronic nature of oxidation-reduction be shown experimentally?
4. What is meant by oxidation-reduction potential?

5. What is meant by an ion-electron partial equation?
6. How do the oxidation-reduction reactions of complex oxidizing and reducing agents differ from those of simple ionic substances?
7. Write ion-electron partial equations to illustrate the reduction of oxyanions in acidic solution; in basic solution.
8. Write ion-electron partial equations to represent the oxidation of nonmetals and oxyanions in acidic and in basic solutions.
9. Employing ion-electron partial equations to show the behavior of the oxidizing and reducing agents, derive the complete equation for the oxidation of each of the reducing agents by each of the oxidizing agents listed below.
   Reducing agents: Cu, Fe, Hg_2^{++}, Fe^{++}, I^-, S^{--}, P, I_2, SO_3^{--}.
   Oxidizing agents: HClO, HNO_3, $KMnO_4$ (acidic solution).
10. Under what conditions is a basic solution favorable for oxidation-reduction? Illustrate by equations.
11. How are hypochlorites prepared industrially? Discuss the reactions of hypochlorous acid, and indicate its uses.
12. What is meant by auto-oxidation-reduction? Explain the changes which occur when a solution of an hypochlorite is warmed.
13. How is potassium chlorate prepared industrially?
14. Discuss the oxidizing activity of the oxyacids of the halogens.
15. What are peroxy compounds? Show by electronic formulas the difference between hydroxides and peroxy compounds; between peroxides and dioxides of metals.
16. What two methods are used for the preparation of hydrogen peroxide?
17. Write equations to indicate that hydrogen peroxide may act as both an oxidizing agent and a reducing agent. How is this fact explained?

SUPPLEMENTARY READINGS

Hammett, L. P., *Solutions of Electrolytes*, McGraw-Hill Book Company, Inc., New York, 1936, chap. VI.

Kelsey, E. B., and H. G. Dietrich, *Fundamentals of Semimicro Qualitative Analysis*, The Macmillan Company, New York, 1940, chap. VIII.

Furnas, C. C., *Rogers Manual of Industrial Chemistry*, D. Van Nostrand Company, New York, 1942, chap. II.

Reichert, J. S., "Hydrogen Peroxide," *Chem. Eng. News* **21**, 480 (1943).

White, J. F., M. C. Taylor, and G. P. Vincent, "Chemistry of Chlorites," *Ind. Eng. Chem.* **34**, 782 (1942).

Chapter 20

SULFUR. SULFURIC ACID

Mention of brimstone, the stone that burns, is made in the literature of early times. This material, the element sulfur, was considered by some alchemists to be an essential ingredient of all combustible substances. Sulfur is in Group VI of the periodic system, with oxygen, selenium, and tellurium. The atoms of these elements contain six valence electrons and enter into reactions to form compounds in various states of oxidation, except that oxygen is assigned an oxidation number of 2 − in its common compounds. The most important oxidation states of sulfur, selenium, and tellurium are 2 −, 4 +, and 6 +. The oxidation number 2 − represents electrovalence in some compounds and covalence in others, but the positive oxidation numbers always represent covalences.

These elements are nonmetallic in nature and exhibit corresponding reactions. As in the halogen group, the elements of higher atomic numbers have lower chemical activity. Sulfur and its compounds are very important, and, consequently, this chapter deals primarily with them, but brief mention is made of selenium and tellurium at the end of the chapter.

Occurrence of Sulfur. Elementary sulfur occurs in regions of volcanic activity in various parts of the earth, *e.g.*, Sicily, Mexico, Iceland, and Japan. The most important deposits in the United States are in the salt domes of Texas and Louisiana. Sulfur in these deposits is not the product of volcanic activity, and its origin is not definitely known. Sulfur also occurs extensively in compounds, *e.g.*, the sulfides of metals such as iron, copper, zinc, and lead; the sulfates of calcium, magnesium, barium, and strontium; and many complex substances of organic origin.

Extraction of Sulfur from Natural Deposits. Prior to 1900, the Sicilian deposit was the most important source of the world's supply of elementary sulfur. but now, the greatest production is

from deposits in Texas and Louisiana. In Sicily, sulfur occurs mixed with volcanic rock, and this rock is mined and heated in kilns to melt the sulfur which then flows away from it. Sulfur obtained from the kilns may be purified by distillation in iron retorts, the vapors being condensed in large brick chambers. In the cold chamber the vapors condense to form a finely divided yellow solid, known as *flowers of sulfur*. When the temperature of the chamber rises above the melting point of sulfur, a liquid product is obtained. The liquid is allowed to flow into molds where it solidifies, forming a product known as *roll sulfur or brimstone*.

Sulfur occurs in a limestone layer in the salt domes in Texas and Louisiana. These domes have a core of common salt. Above this is a layer of anhydrous calcium sulfate, anhydrite, and above this layer, the sulfur-bearing limestone. The limestone strata lie at a distance of approximately 900 ft. below the surface of the earth, covered by sand, clay, and rock. A process developed by

Fig. 90. Sulfur Well. (*Courtesy of Texas Gulf Sulfur Company, Inc.*)

Frasch about 1904 made these deposits available as a source of sulfur. This process consists in melting sulfur from the rock and forcing it to the surface by means of compressed air. Borings are made through the overlying material and four concentric pipes

are driven down into the sulfur deposit. (Fig. 90.) The largest of these pipes is about 8 in. in diameter. Water, superheated under pressure to about 180°, is pumped down through the two outer pipes. Sulfur melts from the deposit at 114.5° and collects in the cavity around the ends of the pipes. When a sufficient quantity of molten sulfur has collected, hot compressed air is forced down the inner pipe, causing the formation of a froth of sulfur, water, and air, which under the increased pressure rises through the remaining pipe. The liquid sulfur is allowed to flow into large wooden bins, where it solidifies in large masses, some containing as much as 100,000 tons. Some of the sulfur wells produce 500 tons per day, and the purity of the product is about 99.5 per cent. The production of sulfur in the United States in 1943 is estimated* as approximately 2,570,000 long tons.

Production of Sulfur from Compounds. Elementary sulfur is recovered as a by-product of certain other processes. This is particularly important in countries with no extensive deposits of elementary sulfur. Large quantities of sulfur have been produced at coke plants and gasoline hydrogenation plants in Germany, and from copper-iron pyrites in Norway. Presumably, the production from these sources has been greatly increased during the war years. In British Columbia, sulfur is obtained from gases produced in smelting metal sulfide ores. Sulfur is also recovered in the purification of fuel gases.

Properties of Sulfur. Solid sulfur exists in at least two crystalline modifications and as an amorphous, noncrystalline, material. These different forms are known as *allotropes*. Both crystalline varieties are soluble in carbon disulfide, but the amorphous product is insoluble in this liquid. *Rhombic sulfur* is stable at any temperature below 96°, the transition temperature. This form of sulfur is a yellow solid with a specific gravity of 2.07 and a melting point of 112.8°. If rhombic sulfur is kept at a temperature between 96° and its melting point, it gradually changes into monoclinic sulfur. *Monoclinic sulfur* is most easily obtained by melting sulfur and then allowing the liquid to cool slowly. As the molten material solidifies, the monoclinic allotrope separates in long, transparent, needlelike crystals, having a specific gravity of 1.96 and a melting point of

* *Chem. Met. Eng.* **51,** 2, 112 (1944).

119.2°. At ordinary room temperatures, this material slowly changes into the rhombic variety.

Amorphous sulfur may be obtained by cooling liquid sulfur quickly from a temperature near the boiling point. A transition in the molecular form of sulfur takes place when the liquid substance is heated. When sulfur is first melted, a straw-colored, readily flowing liquid is obtained. The liquid becomes darker in color and more viscous as the temperature is raised. It is so viscous at about 200° that it flows only very slowly from an inverted test tube. The liquid becomes more fluid as the temperature is raised further and boils at 444.6°. The two molecular allotropes of liquid sulfur are known as $S\lambda$ and $S\mu$, probably S_8 and S_6, respectively. The equilibrium mixture contains 3.6 per cent of $S\mu$ at 120° and about 35 per cent at 444.6°. An elastic mass, known as plastic sulfur, is obtained by pouring sulfur near the boiling point into cold water. This material is a supercooled liquid solution containing two molecular varieties of sulfur. Crystalline material separates from the supercooled solution in a day or two, and may be dissolved in carbon disulfide, leaving a residue of amorphous sulfur. The transition of amorphous into rhombic sulfur occurs very slowly at room temperature.

The temperature at which sulfur is observed to melt is not usually the true melting point, because the liquid in contact with the solid is a solution of the two molecular modifications in each other. This causes a lowering of the melting point, and monoclinic sulfur in contact with this equilibrium mixture melts at 114.5°.

Finely divided sulfur is often produced by the decomposition of sulfur compounds in a form which does not settle and is not easily removed from the solution by filtration. The oxidation of sulfides by nitric acid often produces sulfur in this state. It is also produced by the reaction of polysulfides and certain other complex products with acids. The material is nearly white when first formed and is known as milk of sulfur.

Reactions of Sulfur. Molecular weight determinations, based on the properties of solutions in carbon disulfide, indicate that the molecular modification is S_8 in both crystalline allotropes. The molecular constitution of the solid element is not an important consideration in chemical reactions. Consequently, as a matter of convenience, the uncombined element is represented by the symbol

S. The atomic weights of the isotopes of sulfur are 32, 33, 34, and 36. The relative abundance of these isotopes is such as to give an average value of 32.06, the chemical atomic weight.

The atomic number of sulfur is 16, so that its atoms contain six valence electrons. The element shows a tendency to gain two additional electrons, thus forming the electrovalent sulfide ion, S^{--}. Sulfur unites directly with the common metals, except gold and platinum. Metals that form ions in more than one oxidation state commonly yield the low state in reaction with sulfur.

$$2\,Cu + S \longrightarrow Cu_2S$$
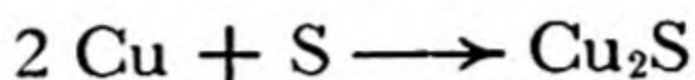
Sulfur burns when it is heated in an atmosphere of hydrogen, forming hydrogen sulfide gas, a molecular product.

$$H_2 + S \longrightarrow H_2S$$
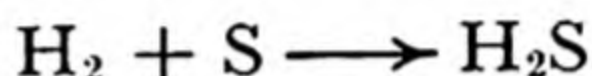
Sulfur also unites with most of the other nonmetallic elements, forming molecular products. The oxidation number of sulfur is $2-$ in these products, except in compounds with oxygen and the halogens.

$$2\,P + 3\,S \longrightarrow P_2S_3$$
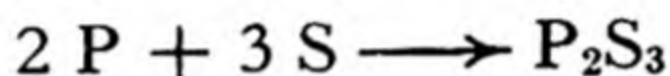
The direct union of sulfur with oxygen produces sulfur dioxide as the principal product of combustion. A small percentage of sulfur trioxide is also formed during the combustion of sulfur.

$$S + O_2 \longrightarrow SO_2$$
$$2\,S + 3\,O_2 \longrightarrow 2\,SO_3$$
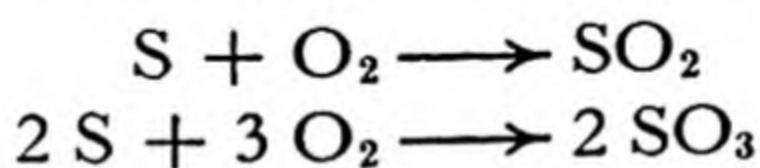
Sulfur has positive oxidation numbers in its oxides and other oxy-compounds.

Uses of Sulfur. Sulfur has a number of industrial uses, the most important being in the production of sulfuric acid and other chemicals. Finely divided sulfur destroys fungi on fruit trees and vines, and it is used in the preparation of fungicide sprays, such as lime-sulfur spray. Sulfur is used in the vulcanization of rubber, the manufacture of matches, and the preparation of dyes. Formerly, sulfur was essential for military purposes in the making of black gunpowder, a mixture of potassium nitrate, sulfur, and charcoal. Although black gunpowder no longer has important military uses, sulfur is nevertheless essential, for it is required in the manufacture of sulfuric acid necessary in the preparation of modern high explosives.

The discovery of the vulcanization of rubber was made by Goodyear in 1839, when he accidentally dropped a mixture of gum rubber and sulfur on a hot stove. He found that the product retained the desired elasticity and acquired strength and many other useful properties, while at the same time the stickiness, which had prevented extensive commercial application, disappeared. Sulfur reacts with compounds present in raw rubber when the mixtures are heated at temperatures of 120–200°. The properties of the product depend on the proportions of sulfur and the temperature and length of time in the vulcanizing process.

Hydrogen Sulfide. This substance occurs free in the water of sulfur springs and in volcanic gases. It is formed by the decay of organic matter in the absence of a sufficient supply of air to cause complete oxidation. The odor of rotten eggs is due partly to hydrogen sulfide.

Preparation of Hydrogen Sulfide. Although hydrogen sulfide results from the direct union of hydrogen and sulfur, it is commonly prepared by the action of acids, which do not possess active oxidizing properties, on metal sulfides such as ferrous sulfide.

$$FeS + 2\,H^+ \longrightarrow Fe^{++} + H_2S \uparrow$$
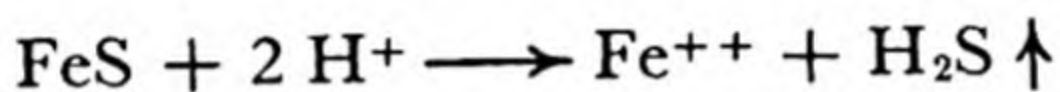
Hydrochloric acid is commonly used for this reaction, but dilute sulfuric acid may be used also. Nitric acid and concentrated sulfuric acid are not suitable because of their strong oxidizing properties.

Properties of Hydrogen Sulfide. Hydrogen sulfide is a gas at ordinary temperatures. The melting point of hydrogen sulfide is − 82.9°, and the boiling point is − 61.8°. The critical temperature is 100.4°. The substance may be stored conveniently as a liquid in steel cylinders. The gas is moderately soluble in water, about three volumes to one of water at room temperature and pressure. Hydrogen sulfide is very poisonous, 1 part in 200 parts of air is likely to prove fatal if breathed for any considerable length of time.

Reactions of Hydrogen Sulfide. The gas burns in air with the formation of water and sulfur dioxide if combustion takes place with an excess of air.

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$
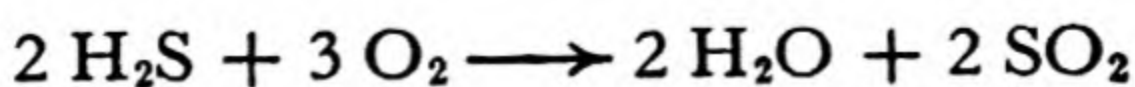
Water and free sulfur are the products of incomplete combustion with limited proportions of air.

$$2 H_2S + O_2 \longrightarrow 2 H_2O + 2 S$$
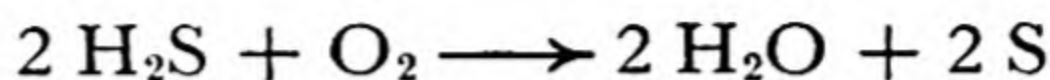
Hydrogen sulfide in aqueous solution is a weak acid, which may give up two hydrogen ions per molecule. The ionization constant for the first stage is 1.1×10^{-7}.

$$H_2S \rightleftharpoons H^+ + HS^-$$
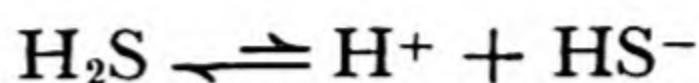
The constant for the secondary ionization is 1×10^{-15}

$$HS^- \rightleftharpoons H^+ + S^{--}$$
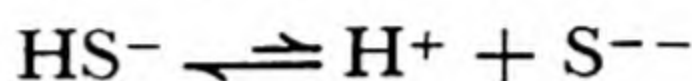
The acid reactions of hydrogen sulfide are not important, except in the preparation of some of the soluble metal sulfides. Sodium hydrogen sulfide is formed by saturating a solution of sodium hydroxide with hydrogen sulfide.

$$H_2S + OH^- \rightleftharpoons H_2O + HS^-$$
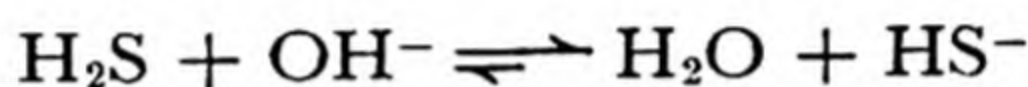
The normal sulfide is formed by adding an equivalent quantity of sodium hydroxide to the solution of the hydrosulfide.

$$HS^- + OH^- \rightleftharpoons H_2O + S^{--}$$
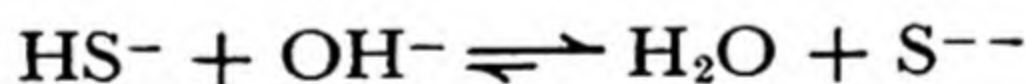
The sulfide ion is a strong base, and the soluble metal sulfides hydrolyze to form strongly basic solutions.

The sulfide ion reactions of hydrogen sulfide cause the precipitation of the slightly soluble metal sulfides when the gas is passed into solutions containing the appropriate ions. Hydrogen sulfide reacts with a solution of a cupric salt, precipitating cupric sulfide.

$$Cu^{++} + H_2S \longrightarrow CuS \downarrow + 2 H^+$$
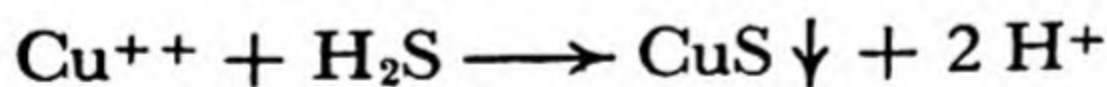
The concentration of sulfide ions is greatly affected by changes in the concentration of hydrogen ions, with the result that a number of the metal sulfides cannot be precipitated from acidic solutions of their ions. This effect and its applications in the use of hydrogen sulfide as an analytical reagent are discussed in Chapter 18, page 289.

A simple test for the presence of hydrogen sulfide is based on the formation of insoluble lead sulfide. A piece of filter paper moistened with a solution of lead nitrate or lead acetate is held in contact

with the gas to be tested, and if hydrogen sulfide is present, a black deposit of lead sulfide is formed.

$$Pb^{++} + H_2S \rightleftharpoons PbS \downarrow + 2\,H^+$$
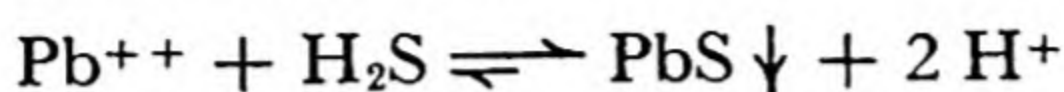
Solutions of hydrogen sulfide have mild reducing properties, due to the presence of sulfide ions in low concentration. Sulfur is precipitated in the reaction of hydrogen sulfide with a halogen, and hydrohalic acid is formed.

$$H_2S + I_2 \longrightarrow S + 2\,I^- + 2\,H^+$$
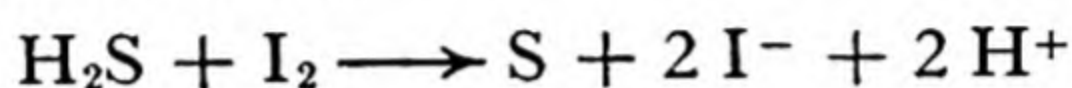
Sulfur Dioxide. This oxide is the principal product of the combustion of sulfur and its compounds. It occurs naturally in volcanic gases.

Preparation of Sulfur Dioxide. Sulfur dioxide is produced commercially by the combustion of sulfur and of sulfides such as zinc sulfide.

$$S + O_2 \longrightarrow SO_2$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$
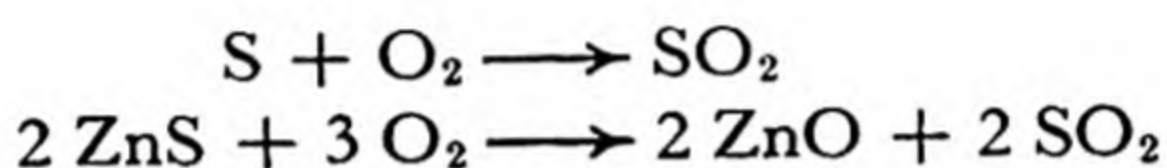
Formerly, the combustion of iron pyrites, FeS_2, was the leading source of sulfur dioxide.

$$4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2$$
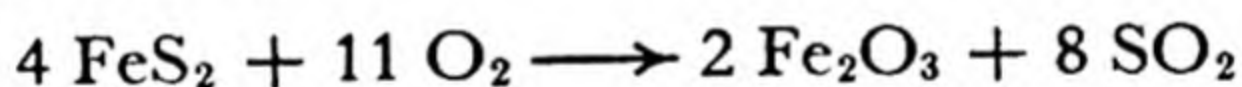
The first step in the production of some metals from naturally occurring sulfide ores is to burn the sulfide, with the formation of the metal oxide and sulfur dioxide as a by-product.

Sulfur dioxide is usually prepared in the laboratory by the reaction of hydrochloric acid with sodium sulfite. Sulfurous acid, the direct product of the ionic reaction, is weakly ionized and is unstable in concentrated solutions at room temperatures.

$$2\,H^+ + SO_3^{--} \rightleftharpoons H_2SO_3$$
$$H_2SO_3 \rightleftharpoons H_2O + SO_2 \uparrow$$
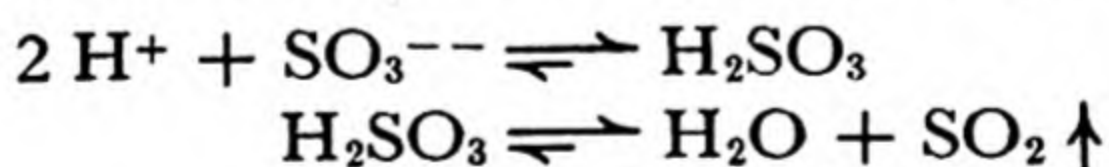
The gas may be collected by the upward displacement of air.

Properties of Sulfur Dioxide. Sulfur dioxide is a gas with a disagreeable odor. The gas is easily liquefied by passing it through a tube immersed in a mixture of ice and salt. The boiling point of the liquid sulfur dioxide is $-10°$, the freezing point, $-72.7°$, and the critical temperature, $157.2°$. The liquid is stored in cylinders in which the pressure at $20°$ is about three atmospheres. The

solubility of the gas is about fifty volumes to one of water at 20°
and a pressure of the gas equal to one atmosphere.

Reactions of Sulfur Dioxide. Sulfur dioxide reacts with water to
form a solution of sulfurous acid. The reaction is reversible, leading
to a state of equilibrium. The rate of the combination reaction
depends on the concentration of the dissolved sulfur dioxide, which
in turn depends on the pressure of the gas in contact with the
liquid at fixed temperature. The rate of the decomposition re-
action depends on the concentration of the sulfurous acid in solu-
tion.

$$SO_2 \text{ (gas)} \rightleftharpoons SO_2 \text{ (dissolved)} + H_2O \rightleftharpoons H_2SO_3$$
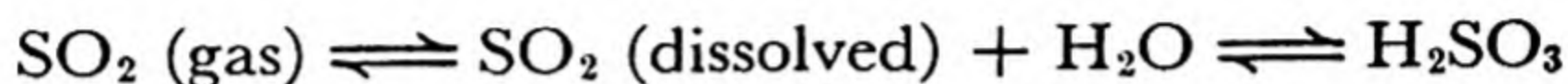
Hence, sulfurous acid decomposes with the evolution of sulfur
dioxide gas in the laboratory preparation of sulfur dioxide when,
due to the reaction of hydrogen and sulfite ions, the concentration
of the molecular acid becomes high.

Sulfur dioxide exhibits other reactions characteristic of acidic
oxides, *viz.*, with basic hydroxides and with basic oxides to form
salts. The most important reaction of sulfur dioxide is with oxygen
to form sulfur trioxide.

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$$
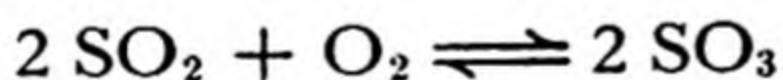
This reaction is discussed in greater detail in connection with the
production of sulfuric acid. When activated by sunlight, sulfur
dioxide reacts with chlorine to form sulfuryl chloride.

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$
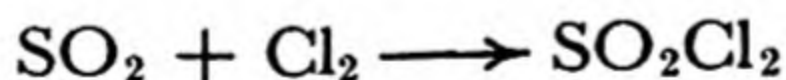
Sulfuryl chloride is a liquid at ordinary temperatures. It is com-
pletely hydrolyzed by hot water with the formation of sulfuric and
hydrochloric acids.

$$SO_2Cl_2 + 2\,H_2O \longrightarrow SO_4{}^{--} + 2\,Cl^- + 4\,H^+$$
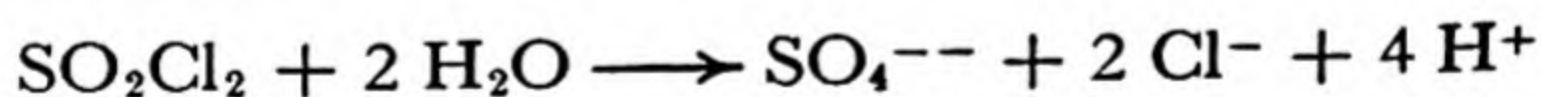
Sulfurous Acid. This substance is a weak acid, which exists only
in solution in equilibrium with sulfur dioxide. The acid yields two
series of salts, the normal sulfites and the hydrosulfites. The hydro-
sulfites contain the anion $HSO_3{}^-$.

$$H_2SO_3 + OH^- \rightleftharpoons HSO_3{}^- + H_2O$$
$$HSO_3{}^- + OH^- \rightleftharpoons SO_3{}^{--} + H_2O$$
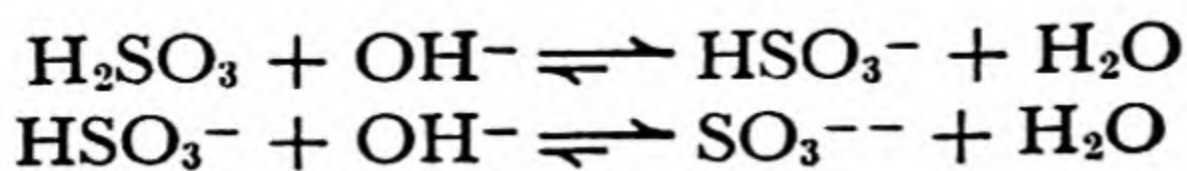
Calcium sulfite is converted into the soluble hydrosulfite by reaction with water and sulfur dioxide.

$$CaSO_3 + H_2O + SO_2 \longrightarrow Ca^{++} + 2\,HSO_3^-$$
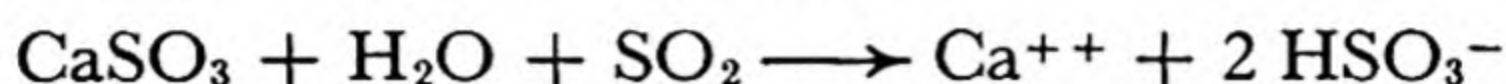
Sulfurous acid reacts slowly with oxygen to form sulfuric acid but reacts rapidly with stronger oxidizing agents such as hypochlorous acid.

$$HClO + H^+ + 2\,\epsilon \longrightarrow H_2O + Cl^-$$
$$\underline{H_2SO_3 + H_2O \longrightarrow SO_4^{--} + 4\,H^+ + 2\,\epsilon}$$
$$HClO + H_2SO_3 \longrightarrow Cl^- + SO_4^{--} + 3\,H^+$$
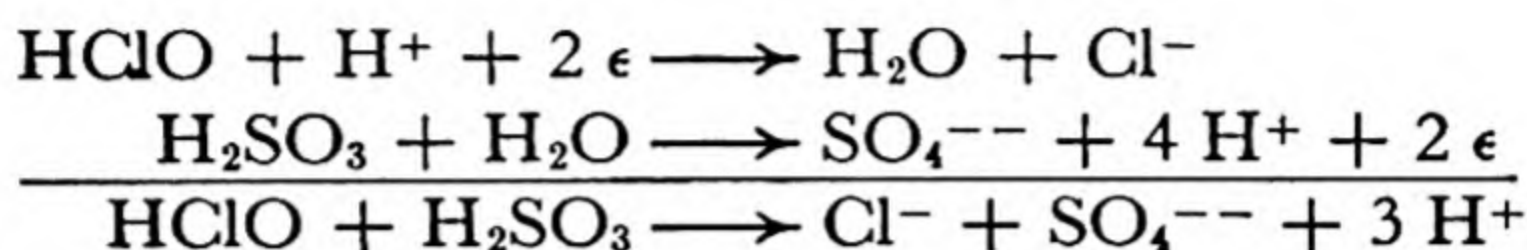
Uses of Sulfur Dioxide. The most important use of sulfur dioxide is in the production of sulfuric acid. Most of the other uses of sulfur dioxide require the presence of water, and the formation of sulfurous acid is usually an intermediate step. Sulfur dioxide is used for the bleaching of some materials, such as wool, silk, and straw, which are damaged by the action of chlorine and hypochlorous acid. Bleaching is due to the formation of colorless products by combination of the color substances with sulfurous acid. Hence materials must be wet for bleaching by sulfur dioxide. Sulfur dioxide is used as a disinfectant in fumigation, and the gas is also used as refrigerant in some household refrigerating machines.

Aside from the production of sulfuric acid, the most extensive use of sulfur dioxide is in the paper industry. Calcium hydrogen sulfite, $Ca(HSO_3)_2$, prepared by the reaction of water and sulfur dioxide with calcium carbonate, is used to cause the disintegration of wood in the formation of wood pulp. Lignin, the cementing material in the wood, is dissolved, the materials are bleached, and a relatively pure form of cellulose is obtained. This product may be used for the manufacture of paper, rayon, and a number of other materials.

SULFURIC ACID

This substance was known in the days of the alchemists, but its manufacture did not reach a commercial stage until 1765. It is the most important of the inorganic chemicals. Because it is used in many processes in large amounts and its production and consumption respond quickly to changes in business activities, it is a good barometer of general business conditions. It has been said

that the industrial development of any country can be estimated from its consumption of sulfuric acid.

Production of Sulfuric Acid. The production of sulfuric acid requires three reactions, *viz.*, the formation of sulfur dioxide by burning sulfur or sulfides, the oxidation of the dioxide to the trioxide, and the reaction of the trioxide with water to form sulfuric acid. These reactions are not carried out separately with isolation of intermediate products but are stages in a single process. The reactions may be carried out consecutively as in the contact process, or the second and third stages may run concurrently as in the lead chamber process. The oxidation of sulfur dioxide to sulfur trioxide requires special conditions for a satisfactory yield.

The Contact Process. The reaction of sulfur dioxide with oxygen is reversible, and the formation of sulfur trioxide is exothermic. A state of equilibrium is established when the materials react in a closed system.

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3 + 45{,}200 \text{ cal.}$$
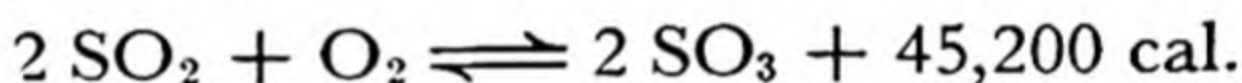
A constant may be derived to represent the concentration relationships at equilibrium. The molar concentrations of gases, *i.e.*, the number of moles in one liter, are small unless high pressures are applied. It is customary to represent the concentration effect for gases by their partial pressures, which are proportional to their concentrations. At constant temperature, the equilibrium proportions bear the ratio shown by the following equation:

$$\frac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}} = K$$

This indicates that an excess of oxygen is a favorable condition for increasing the yield of sulfur trioxide, provided the increased proportion of air, used to supply the excess of oxygen, does not lower the partial pressure of sulfur dioxide too greatly. Likewise, an increase in the total pressure applied to the system gives a greater proportion of sulfur trioxide, the product of smaller volume, in the equilibrium mixture. High pressures are not at present economically profitable, because a large percentage of the sulfur dioxide may be converted to the trioxide without recourse to high pressure.

The velocity of the reaction at ordinary temperatures is too low for industrial operation. Consequently, higher temperatures must

be employed in order to increase the velocity of the reaction. At high temperatures, the yield of sulfur trioxide is greatly decreased, according to van't Hoff's law. (See page 132.) The equilibrium mixture in this system contains about 98 per cent of sulfur trioxide at 400° and a pressure of one atmosphere, 60 per cent at 700°, and
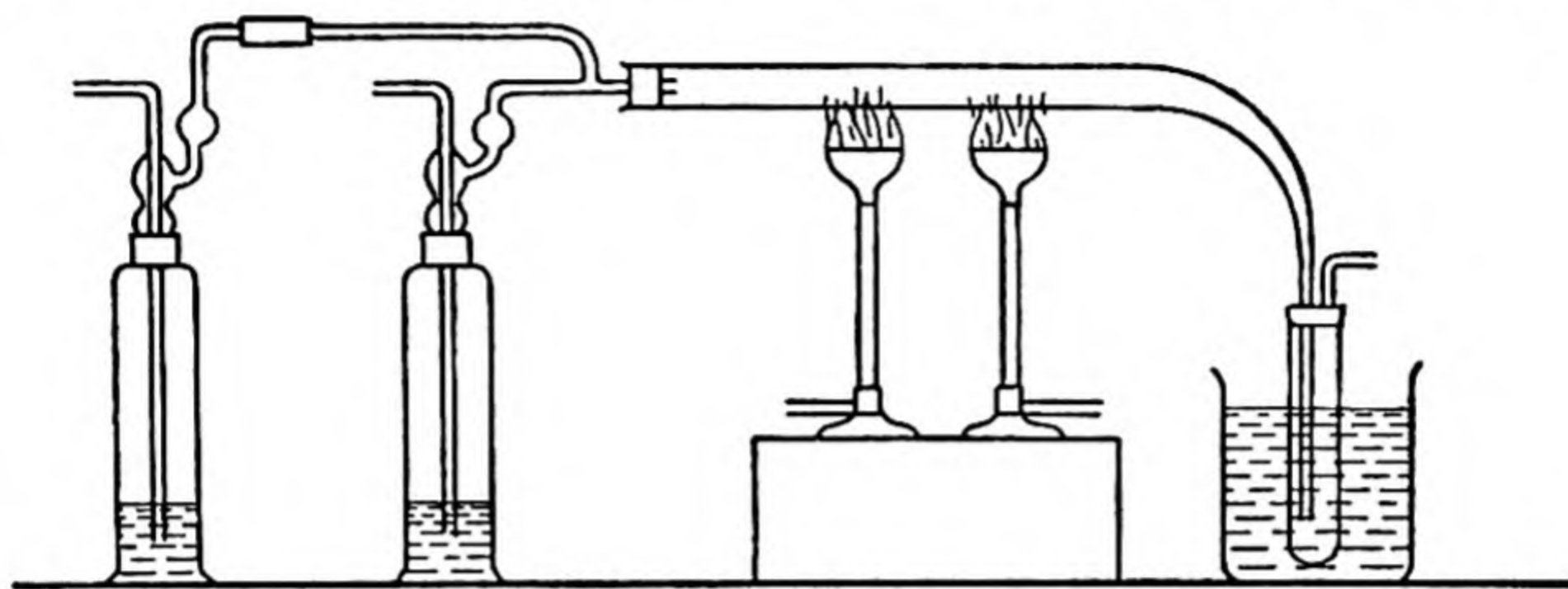
Fig. 91. Laboratory Apparatus for the Preparation of Sulfur Trioxide

very little at 1000°. Platinum is an effective catalyst for this reaction. Since platinum is a contact catalyst in this process, the metal is finely divided to give as large an exposed surface as practical for a small weight of metal. In the laboratory preparation of sulfur trioxide, a mixture of sulfur dioxide and oxygen is passed in contact with finely divided platinum, supported on asbestos fiber or other inactive material (Fig. 91) at a temperature approximately 400°. The product may be condensed by passing the gaseous mixture through a tube surrounded by cold water.
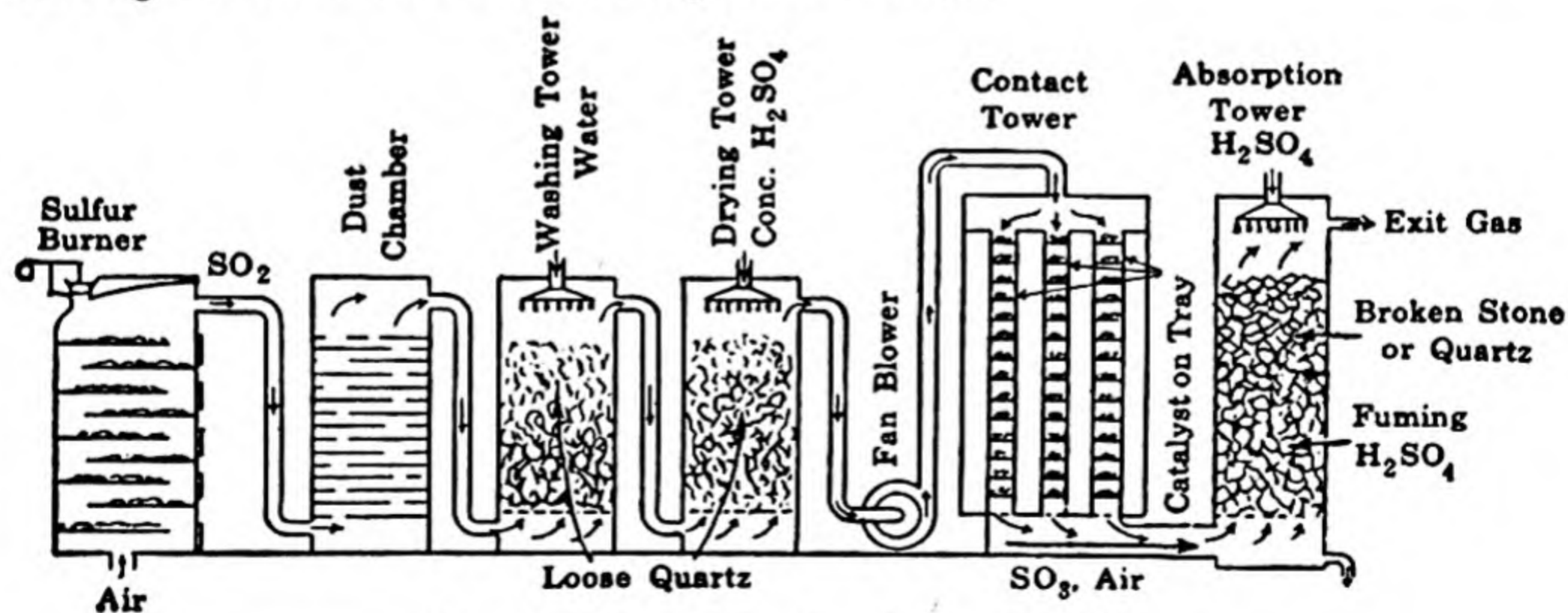
Fig. 92. Diagram of a Contact Process

The steps involved in the industrial process are shown diagrammatically in Fig. 92. A mixture of sulfur dioxide and a moderate

excess of air is passed through the converter in contact with the catalyst at a temperature of approximately 400°. Impurities such as dust and arsenic trioxide, often present in sulfur dioxide produced by burning metal sulfides, "poison" the platinum catalyst, decreasing its effectiveness. Consequently, such materials must be removed from the gas mixture before it is admitted to the converter. Since the reaction of sulfur dioxide with oxygen is exothermic, the temperature tends to rise, decreasing the percentage of sulfur dioxide converted into trioxide. In order to prevent this, the cold gases may be circulated over the pipes containing the catalyst. In this manner, the gas mixture itself is sufficiently preheated to maintain the reaction.

The product of this step in the process is sulfur trioxide in mixture with other gases, chiefly nitrogen and excess of oxygen. Sulfur trioxide is absorbed from this mixture in concentrated sulfuric acid, reacting with the water it contains.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
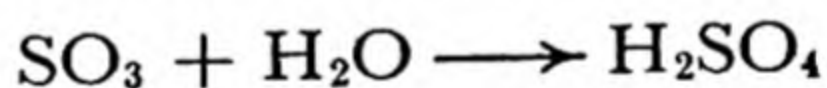
The regulated addition of water maintains the concentration at approximately 98 per cent. If the gas mixture is passed directly
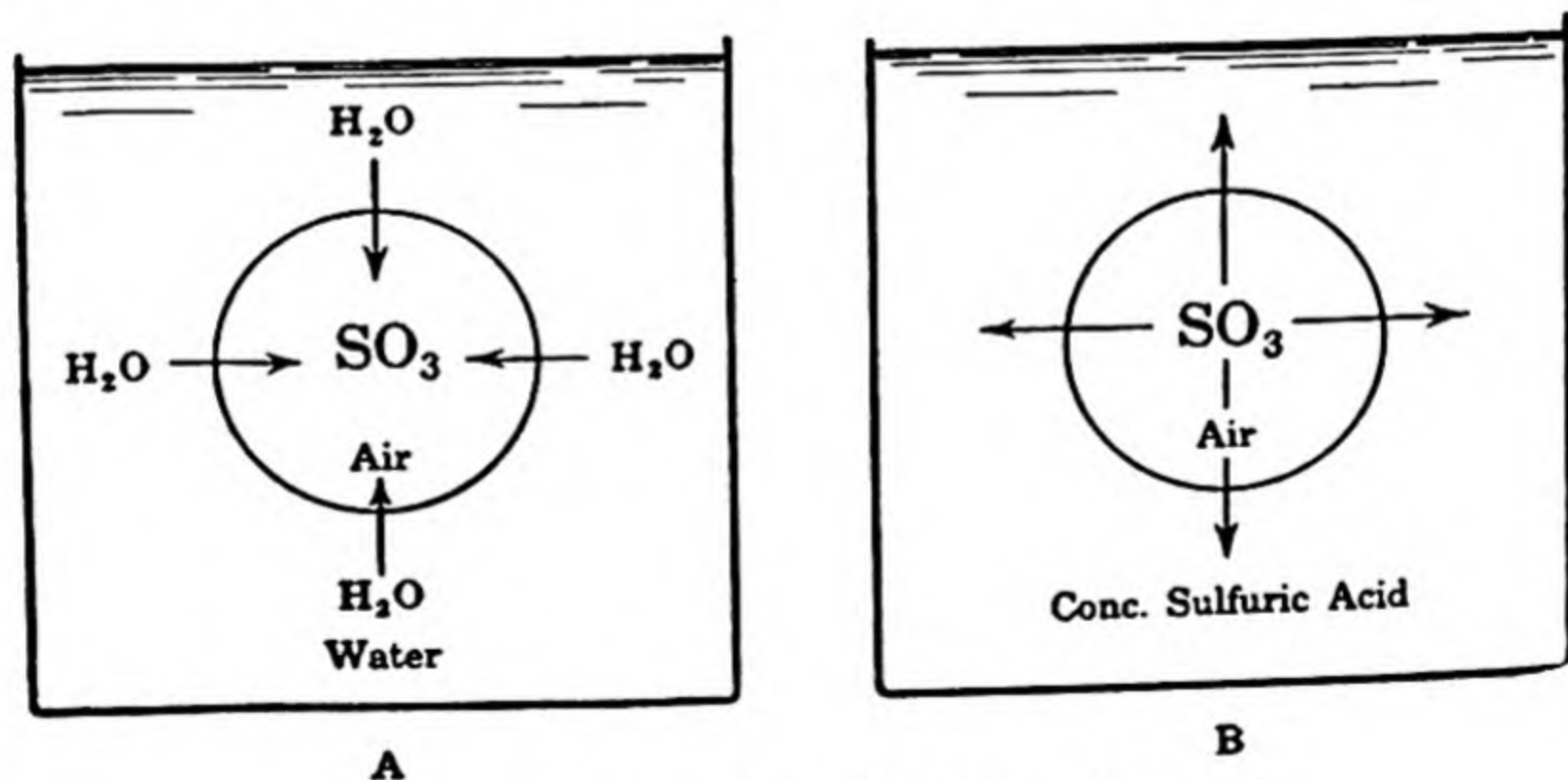
Fig. 93. *Absorption of Sulfur Trioxide*

into water, a fog consisting of minute droplets of sulfuric acid is formed in the gas bubble. The vapor pressure of water is high enough to cause it to evaporate rapidly into the gas bubbles (Fig. 93), and the reaction forming sulfuric acid occurs producing a fog. Because of the low solubility of air in water, a large proportion of the sulfuric acid fog is carried through the liquid. Fog forma-

tion does not occur when the gas mixture is passed into concentrated sulfuric acid, because the vapor pressure of water is so low that no appreciable evaporation into the gas bubbles takes place. Molecules of gaseous sulfur trioxide move much more rapidly than droplets of liquid in the fog. Hence, there is time enough for most of the sulfur trioxide molecules to pass into the solution before the gas bubbles emerge from the absorption towers.

More concentrated sulfuric acid may be produced by stopping the addition of water. After all the water in the concentrated acid has reacted, additional sulfur trioxide may be absorbed forming fuming sulfuric acid, *oleum*, an equilibrium mixture of sulfuric acid, sulfur trioxide, and *pyrosulfuric acid*, $H_2S_2O_7$.

$$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7$$
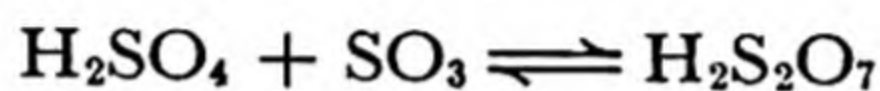
Other catalysts may be used to increase the velocity of the reaction of sulfur dioxide with oxygen. A contact catalyst, consisting primarily of vanadium pentoxide supported by inactive substances, is not significantly affected by some of the substances that are catalyst poisons toward platinum. This catalyst has been in use for a number of years.

Lead Chamber Process. The oxidation of sulfur dioxide is caused in this process by the action of oxygen and nitric oxide. The reactions take place at moderate temperatures as the gas mixture passes slowly through large chambers. In this way the heat of reaction is dissipated so that the temperature does not rise too high and the reactions are nearly complete. The chambers are lined with lead, since this is only superficially attacked by sulfuric acid of the concentration produced in the process. A number of reactions may occur in the chambers, but the essential changes are illustrated by the following equations.

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$
$$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 + NO$$
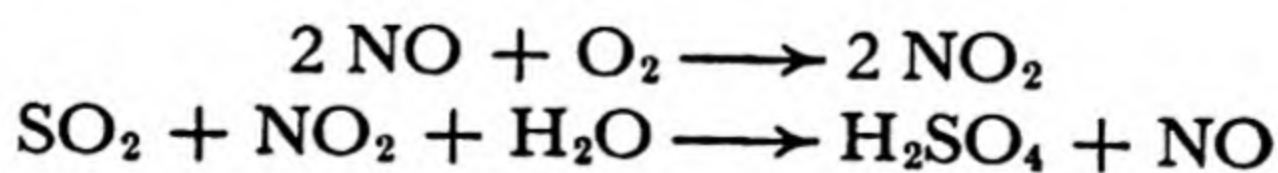
Nitric oxide is known as a *carrier catalyst* in this reaction. A small proportion of the catalyst with an excess of oxygen is sufficient to cause the oxidation of large proportions of sulfur dioxide. Both of these reactions occur rapidly at moderate temperatures, whereas the direct reaction of sulfur dioxide with oxygen occurs only slowly.

The essential steps in this process are indicated diagrammatically in Fig. 94.

It is important that oxides of nitrogen be recovered from the waste gases and returned to the chambers. This may be accom-
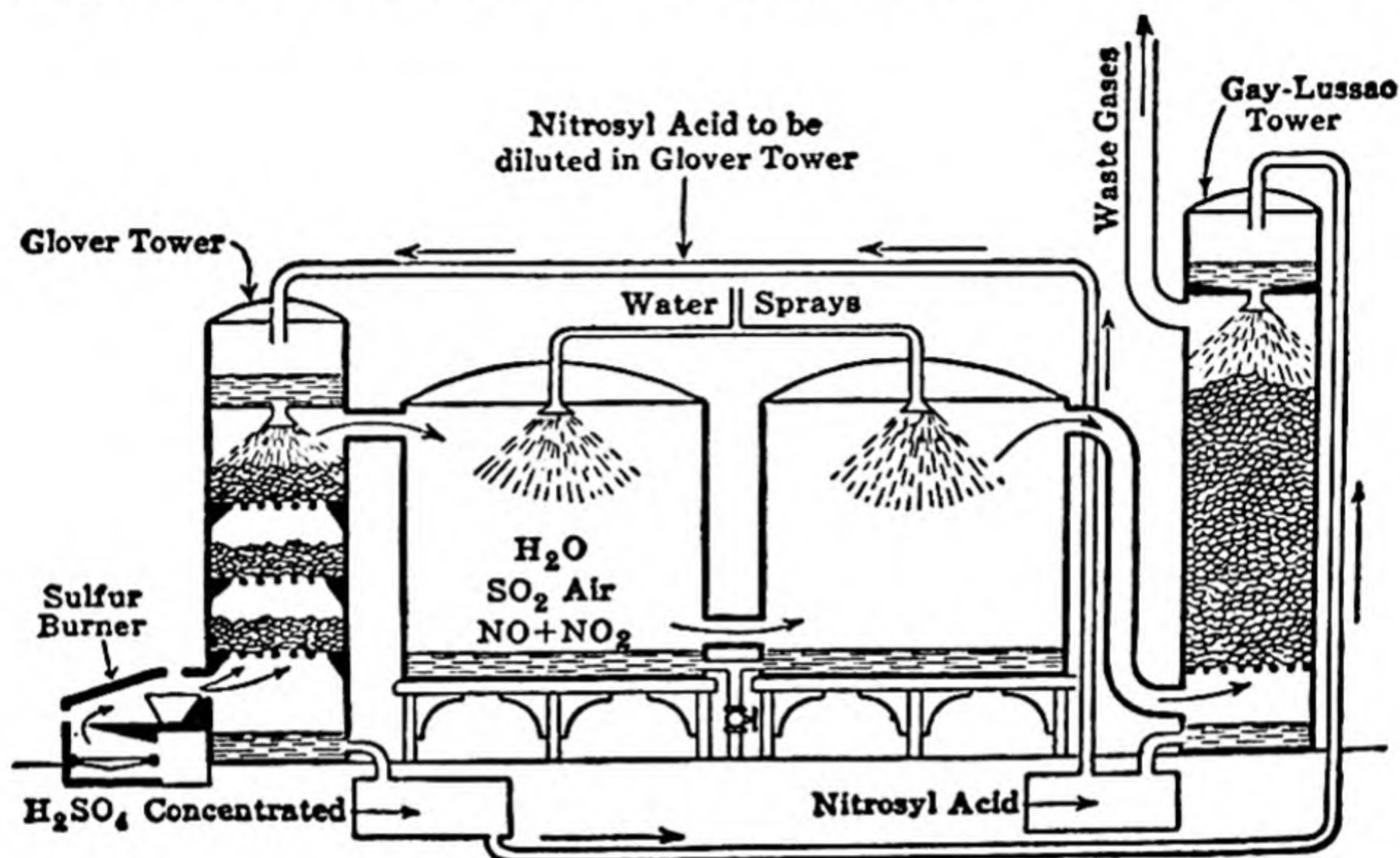
Fig. 94. Diagram of Lead Chamber Plant

plished by absorbing nitrogen dioxide in concentrated sulfuric acid, trickling over inactive material in the Gay-Lussac tower. The product of this reaction is known as *nitrosyl sulfuric acid.*

$$H_2SO_4 + 2NO_2 \longrightarrow HNOSO_4 + HNO_3$$
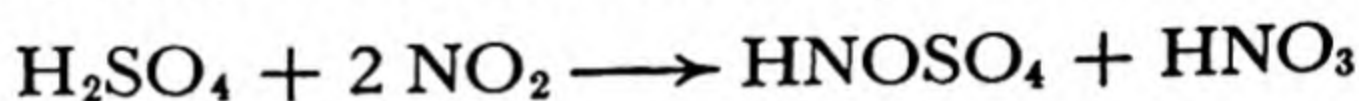
This acid mixture is forced to the top of the Glover tower, where it is diluted with water or with the chamber acid as it is admitted. As it passes down through this tower, the acid meets a counter-current of the gas mixture of sulfur dioxide and air coming from the sulfur burners. Nitric oxide is formed and joins the gases passing into the chambers.

$$2HNOSO_4 + SO_2 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$$
$$2HNO_3 + 3SO_2 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$$
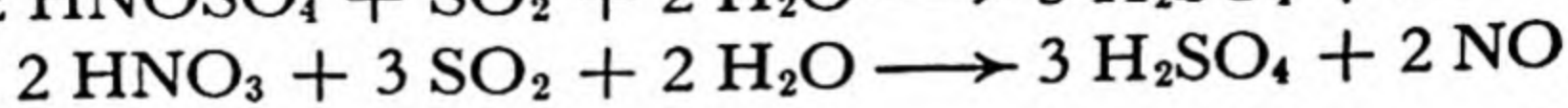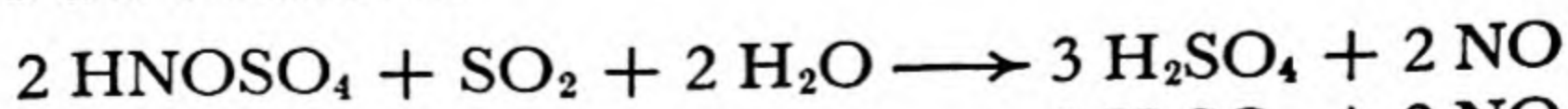
The most concentrated product of the process is the acid which collects in the reservoir at the base of the Glover tower.

Although nitric oxide is recovered in this process, there is some mechanical loss due to incomplete absorption in concentrated sulfuric acid. Consequently, nitric oxide must be admitted along

with the other gases to compensate for this loss. This additional supply is now produced at most chamber plants by the oxidation of ammonia. (See page 346.)

Comparison of the Two Processes. The two processes supplement each other in supplying the industrial demand for sulfuric acid. The acid from the contact process is the more nearly pure and may be made in any desired concentration up to fuming acid. The purification of the gases, necessary to prevent poisoning of the platinum catalyst, adds to the cost of production. The main product of the chamber process contains many impurities and has a concentration of only 60–65 per cent of sulfuric acid. The purification and concentration of the chamber acid increases the cost of production. There are a number of uses for the more dilute product in which the presence of impurities is of no consequence. For such uses the lead chamber process has been the cheaper, while the contact process is better for producing pure concentrated sulfuric acid. The use of the vanadium catalyst dispenses with purifying the gases to prevent poisoning of the catalyst, and makes it possible for the contact process to produce the dilute acid in competition with the lead chamber process.

Properties of Sulfuric Acid. Sulfuric acid is a colorless oily liquid with a specific gravity of 1.83. The pure compound decomposes when it is heated, with the evolution of sulfur trioxide and the formation of a constant boiling solution. This solution contains 98.3 per cent of sulfuric acid and boils at 338° under a pressure of 760 mm. The acid dissolves in water in all proportions, and heat is evolved in the process. The acid and water react with each other, and the solution shows a great departure in vapor pressure effects from the ideal solution. (See page 115.) The vapor pressure of water in equilibrium with concentrated sulfuric acid is low. This is attributed to the formation of stable hydrates, which require only small proportions of uncombined water for equilibrium.

Sulfuric Anhydride. Sulfur trioxide, SO_3, is the anhydride of sulfuric acid. It may be isolated as the product of the oxidation of sulfur dioxide in the contact process. It is a colorless liquid with a freezing point of 15° and a boiling point of 46°. The solid soon changes to a mass of needle-shaped crystals, in which the substance has the molecular composition represented by the formula, S_2O_6,

a polymer of sulfur trioxide. The solid sublimes when it is warmed. Sulfur trioxide reacts with water to produce a number of hydrates represented by the formulas: $SO_3(H_2O)$, H_2SO_4; $(SO_3)_2(H_2O)$, $H_2S_2O_7$; $SO_3(H_2O)_2$; $SO_3(H_2O)_3$; $SO_3(H_2O)_5$. These substances may be crystallized from solution as products having definite composition.

Reactions of Sulfuric Acid. Concentrated sulfuric acid combines with water to form the stable hydrates noted in the preceding paragraph. Because of this property, the concentrated acid is a good *dehydrating agent*. It not only is a good drying agent for gases with which it does not react, but it also takes up hydrogen and oxygen from many compounds in the proportions of water. Thus, cellulose, represented by the empirical formula $C_6H_{10}O_5$, is decomposed by hot concentrated sulfuric acid, leaving a residue of carbon. Ethyl alcohol, C_2H_5OH, may be dehydrated to form ether, $(C_2H_5)_2O$, an anaesthetic, or the hydrocarbon ethylene, C_2H_4, depending on the temperature of the reacting materials.

Because of its high boiling point, sulfuric acid reacts with salts of acids of lower boiling point. The concentrated acid is added to the salt, and the mixture is heated as required to drive out the acid of lower boiling point. Either the normal sulfate or the hydrosulfate, commonly called the bisulfate, may be produced in this reaction, depending on the proportions of the acid and salt, and the temperature employed. The following equations represent the preparation of acetic acid, hydrochloric acid, and nitric acid, respectively, from their salts.

$$2\,NaC_2H_3O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HC_2H_3O_2 \uparrow$$
$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl \uparrow$$
$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3 \uparrow$$
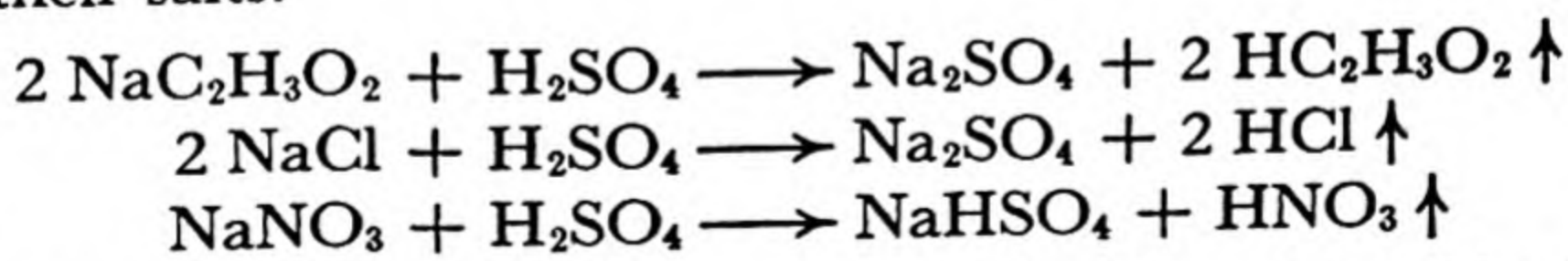
Sulfuric acid ionizes in aqueous solution. The first stage of ionization is nearly complete in dilute solution, but the second stage is not complete

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$$
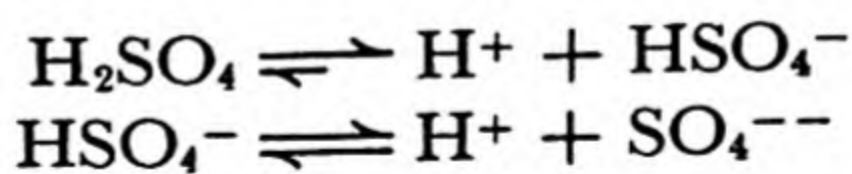
Sulfuric acid solutions exhibit two series of reactions, the reactions of hydrogen ions and the reactions of sulfate ions.

Due to hydrogen ions, sulfuric acid exhibits the usual acid reactions previously represented in nonionic form for hydrochloric acid.

(See page 171.) Either normal sulfates or hydrosulfates may be separated from the solution, depending on the proportions of acidic and basic substances.

$$H^+ + OH^- \rightleftharpoons H_2O$$
$$2\,H^+ + MgO \longrightarrow H_2O + Mg^{++}$$
$$2\,H^+ + CO_3^{--} \longrightarrow H_2O + CO_2 \uparrow$$
$$H^+ + NH_3 \rightleftharpoons H_2O + NH_4^+$$
$$2\,H^+ + Zn \longrightarrow H_2 \uparrow + Zn^{++}$$
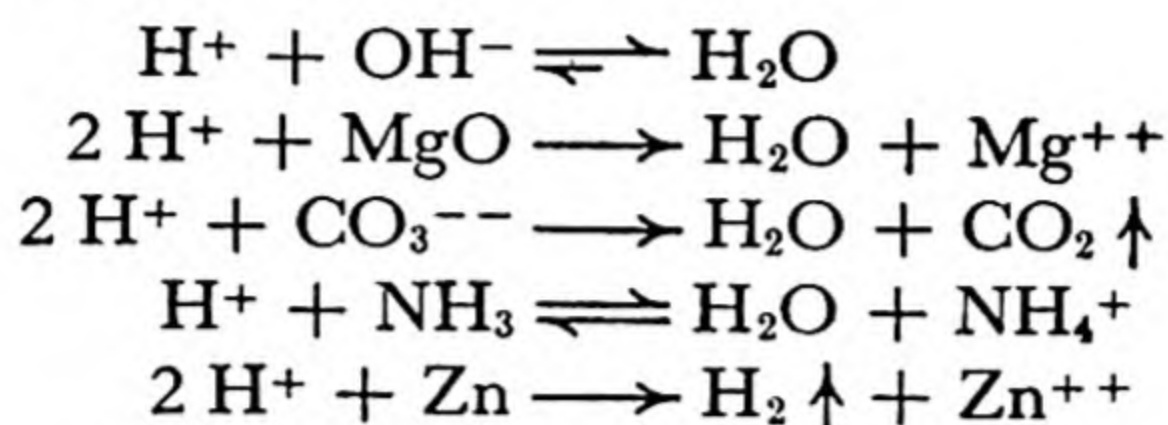
The reaction of sulfuric acid with insoluble phosphates, such as calcium phosphate, produces the soluble dihydrogen phosphate extensively used in fertilizers. With the correct proportions of the materials, a mixture of the solid phosphate and the hydrated sulfate is produced.

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 + 4\,H_2O \longrightarrow Ca(H_2PO_4)_2 + 2\,CaSO_4(H_2O)_2$$
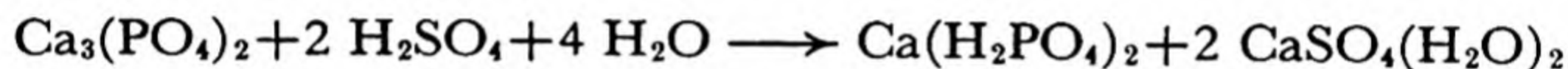
Due to sulfate ions, solutions of sulfuric acid react with the ions of metals yielding insoluble sulfates. With the exception of the sulfates of barium, strontium, and lead, the sulfates are soluble, although the solubility of calcium sulfate and silver sulfate is not high.

$$Ba^{++} + SO_4^{--} \rightleftharpoons BaSO_4 \downarrow$$
$$Sr^{++} + SO_4^{--} \rightleftharpoons SrSO_4 \downarrow$$
$$Pb^{++} + SO_4^{--} \rightleftharpoons PbSO_4 \downarrow$$
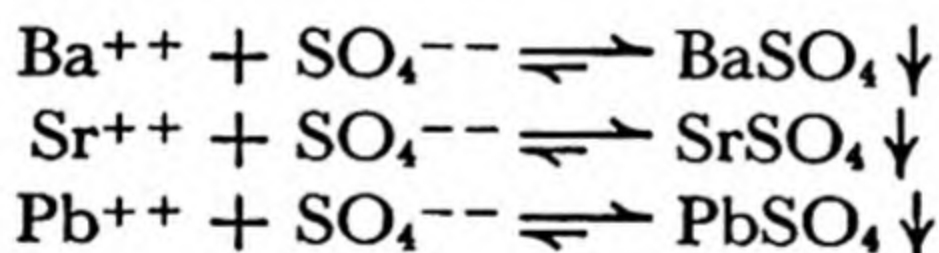
The test for the presence of sulfate ions in solution of sulfuric acid and other soluble sulfates is based on the reaction with a solution of barium chloride to form a white precipitate of barium sulfate, which is not soluble in dilute hydrochloric acid. A number of the negative ions yield precipitates with barium salts in neutral or basic solution, *e.g.*, carbonate, phosphate, sulfite, and borate. In the presence of an acid, however, the concentration of these anions is reduced because they are the ions of weak acids.

$$PO_4^{---} + 2\,H^+ \rightleftharpoons H_2PO_4^-$$
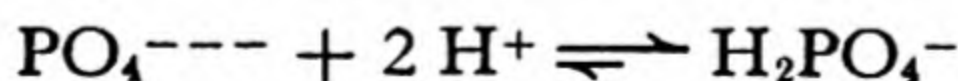
In this way, the concentration of the phosphate ion is reduced so greatly that the product of the molar concentrations of the barium and phosphate ions raised to the proper powers is less than the solubility product of barium phosphate.

$$[Ba^{++}]^3 \times [PO_4^{---}]^2 < S_{Ba_3(PO_4)_2}$$

Barium phosphate does not precipitate, and a similar condition exists in solutions of the other anions mentioned above. Sulfuric acid, however, is a strong acid, and the addition of dilute hydrochloric acid to a solution of a sulfate does not greatly affect the concentration of sulfate ions. When a solution of barium chloride is added, the product of the molar concentration of the barium sulfate ions is greater than the solubility product of barium sulfate.

$$[Ba^{++}] \times [SO_4^{--}] > S_{BaSO_4}$$

Therefore, the precipitate of barium sulfate does form.

Oxidizing Action of Sulfuric Acid. Sulfate ions in dilute solution are stable toward reduction. Consequently, the oxidizing activity of dilute sulfuric acid is small. Hot concentrated sulfuric acid is a vigorous oxidizing agent. Several reduction products of sulfuric acid may be formed. The product obtained in any particular reaction depends on the activity of the reducing agent and the rates of the various possible reactions. The usual reduction product of hot concentrated sulfuric acid is sulfur dioxide, though hydrogen sulfide is often produced by the action of strong reducing agents. Concentrated sulfuric acid is a molecular substance, and the protons required in the half reaction for its reduction come from other molecules of the acid.

$$H_2SO_4 + H_2SO_4 + 2\,\epsilon \longrightarrow SO_2 + SO_4^{--} + 2\,H_2O$$
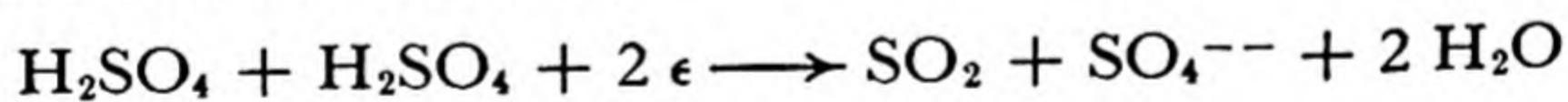
The nature of the oxidation product is the same as in the reaction of other acidic oxidizing agents with reducing agents of different classes. (See page 302.) Metals are oxidized to form their ions. Metallic bismuth, for example, is oxidized by hot concentrated sulfuric acid to form bismuth ions, and the reduction product is sulfur dioxide.

$$[2\,H_2SO_4 + 2\,\epsilon \longrightarrow SO_2 + SO_4^{--} + 2\,H_2O] \times 3$$
$$\underline{[Bi \longrightarrow Bi^{+++} + 3\,\epsilon] \times 2}$$
$$6\,H_2SO_4 + 2\,Bi \longrightarrow 3\,SO_2 + 2\,Bi^{+++} + 3\,SO_4^{--} + 6\,H_2O$$
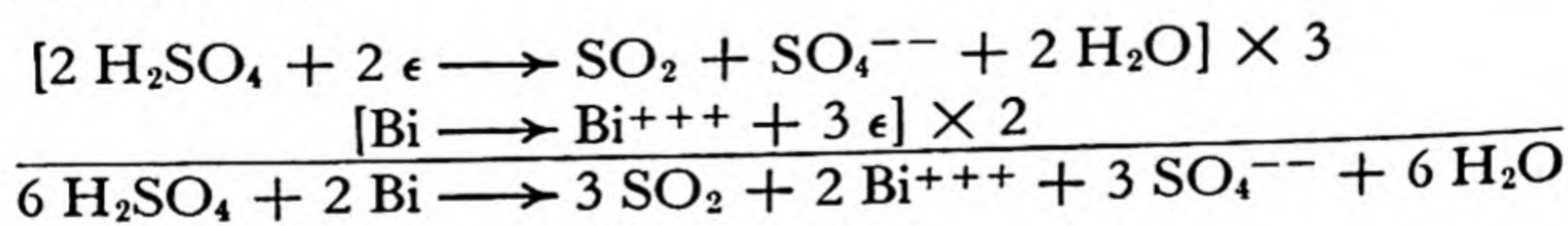
Hot concentrated sulfuric acid oxidizes bromides to bromine.

$$2\,H_2SO_4 + 2\,\epsilon \longrightarrow SO_2 + SO_4^{--} + 2\,H_2O$$
$$\underline{2\,Br^- \longrightarrow Br_2 + 2\,\epsilon}$$
$$2\,H_2SO_4 + 2\,Br^- \longrightarrow SO_2 + SO_4^{--} + Br_2 + 2\,H_2O$$
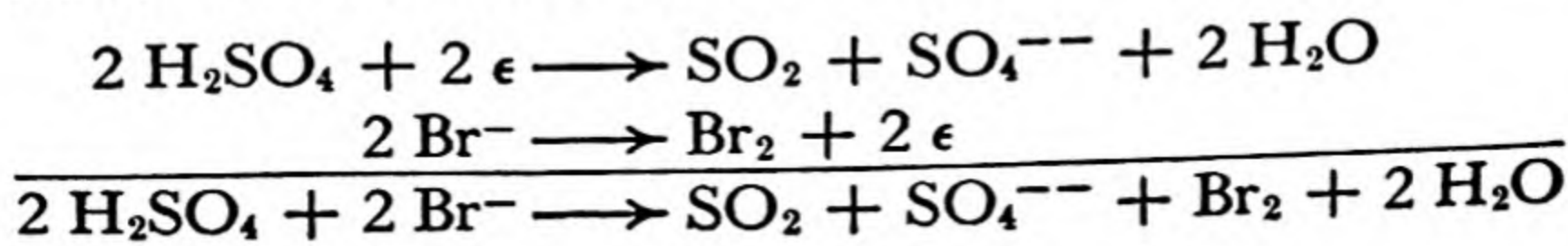
Iodine is less active than bromine, and iodides are better reducing agents than bromides. Hot concentrated sulfuric acid is reduced to hydrogen sulfide by reaction with iodides.

$$5\,H_2SO_4 + 8\,\epsilon \longrightarrow H_2S + 4\,SO_4^{--} + 4\,H_2O$$
$$\underline{[2\,I^- \longrightarrow I_2 + 2\,\epsilon] \times 4}$$
$$5\,H_2SO_4 + 8\,I^- \longrightarrow H_2S + 4\,SO_4^{--} + 4\,I_2 + 4\,H_2O$$
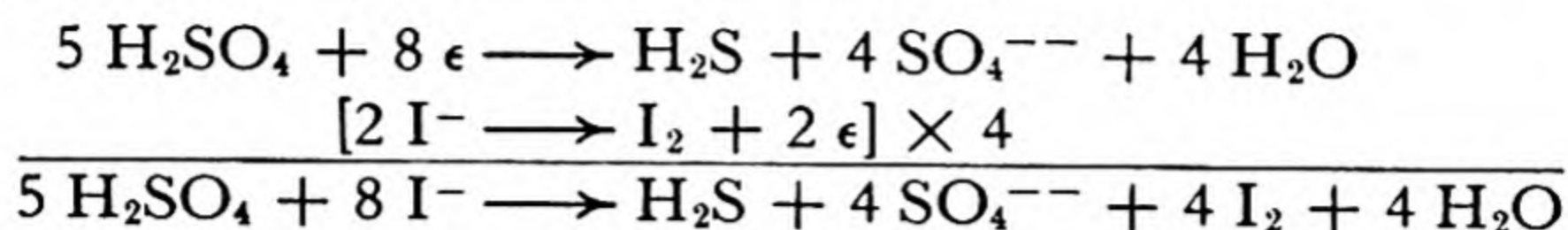
Economic Importance of Sulfuric Acid. The importance of this acid and the prompt response in demand to changes in business conditions are shown by the quantities of sulfuric acid used in the United States in a few selected years: 1930, 7,625,000 tons; 1932, 4,650,000 tons; 1936, 7,632,000 tons; 1940, 9,185,000 tons; 1942, 12,515,000 tons; 1943, 13,917,000 tons. The quantities are in short tons of the 62 per cent acid. The figures for 1942 and 1943 are estimates.*

TABLE 28. DISTRIBUTION OF SULFURIC ACID [a] CONSUMED
IN THE UNITED STATES [b]

(thousands of tons)

Industry	1941	1942	1943
Fertilizer	2,500	2,900	4,100
Petroleum refining	1,400	1,650	1,720
Chemicals and defense [c]	1,790	2,250	2,350
Coal products	940	970	927
Iron and steel	1,500	1,600	1,650
Other metallurgical uses	800	840	860
Paints and pigments	700	760	800
Industrial explosives	190	195	190
Rayon and cellulose film	555	625	635
Textiles	165	145	135
Miscellaneous	500	530	550
Totals	11,040	12,515	13,917

[a] Basis, 50 degree Be., 62.18% of H_2SO_4.
[b] *Chem. Met. Eng.* **51**, 2, 112 (1944).
[c] Production for military explosives is included with chemicals.

This acid is utilized either directly or indirectly in many fundamental industries. Its high boiling point is the basis of its use in the preparation of more volatile acids such as hydrochloric and nitric acids. Due to its acid properties, it is employed in the conversion of natural phosphate rock into soluble acid phosphates suitable for fertilizers, in the manufacture of ammonium sulfate, in cleaning

* *Chem. Met. Eng.* **51**, 2, 112 (1944).

iron and steel to be galvanized or tinned, and in the preparation of sulfates. Sulfuric acid finds extensive application as a dehydrating agent in the manufacture of explosives, dyes, drugs, and many other commercial products. Large quantities of the acid are used in the petroleum industry, due in part to the oxidizing properties that render it suitable for the removal of organic sulfides. This substance has many additional applications but those listed account for the largest part of the total consumption.

Some Additional Oxyacids of Sulfur. There are a number of oxyacids of sulfur in which complex molecules are formed in consequence of electron sharing between two or more sulfur atoms.

TABLE 29. OXYACIDS OF SULFUR

Name	Formula	Name	Formula
Hyposulfurous acid	$H_2S_2O_4$	Dithionic Acid	$H_2S_2O_6$
Sulfurous	H_2SO_3	Trithionic	$H_2S_3O_6$
Sulfuric	H_2SO_4	Tetrathionic	$H_2S_4O_6$
Thiosulfuric	$H_2S_2O_3$	Peroxymonosulfuric	H_2SO_5
Pyrosulfuric	$H_2S_2O_7$	Peroxydisulfuric	$H_2S_2O_8$

Certain of these acids and their salts have specific uses of considerable importance. The sodium salt of hyposulfurous acid, for example, is used commercially for the reduction of indigo, and sodium thiosulfate is used in photographic fixing baths. Pyrosulfuric acid has been mentioned in connection with the contact process. It is a very powerful dehydrating agent. The sodium salt of peroxysulfuric acid is important as an active oxidizing agent. The preparation, properties, and uses of these compounds involve a considerable amount of specific detail which is beyond the scope of this text. Those interested may secure information about these substances from a general treatise on inorganic chemistry.

Similarities of Selenium and Tellurium to Sulfur. Selenium occurs in free condition in some sulfur deposits and in the selenides of copper, silver, and lead. Tellurium occurs primarily in the tellurides of gold, silver, and copper. There are a number of isotopes of each of these elements. The elements may be obtained in several crystalline forms and in the amorphous state. The elements are not scarce and could be produced in moderately large quantities if there were sufficient commercial demand. Selenium is used in the production of ruby red glass, in the vulcanization of some types of

rubber goods, and in the preparation of copper alloys. Small percentages of tellurium may be used in lead to increase its resistance to corrosion.

The hydrides of selenium and tellurium may be prepared by methods similar to those used for the preparation of hydrogen sulfide, *viz.*, the direct union of the elements and the reaction of acids with binary metal compounds. The gases have disagreeable odors and are very toxic. The activity of the elements, sulfur, selenium, and tellurium, decreases with increasing atomic number, and the reducing activity of the ions correspondingly increases.

The dioxides of selenium and tellurium are formed by the combustion of the elements. Selenium dioxide reacts with water to form selenious acid, H_2SeO_3. Tellurium dioxide does not react with water, but yields sodium tellurite, Na_2TeO_3, when fused with sodium hydroxide. Selenic acid, H_2SeO_4, and telluric acid, H_6TeO_6, are formed by the action of strong oxidizing agents on selenium dioxide and tellurium dioxide, respectively. These acids are strong oxidizing agents.

EXERCISES

1. Describe the production of sulfur from the Texas and Louisiana deposits.
2. Describe the allotropic forms of sulfur, and state the conditions under which each is produced.
3. Write equations to represent typical reactions of sulfur.
4. Illustrate by equations reactions of hydrogen sulfide as an acid, as a reducing agent, and as a precipitant.
5. Discuss the equilibria of sulfur dioxide in aqueous solution, indicating the effect on these equilibria of (*a*) heating the solution, (*b*) increasing the pressure of sulfur dioxide gas, (*c*) the addition of a strong acid, (*d*) the addition of a base.
6. What three reactions are involved in the production of sulfuric acid?
7. In terms of the equilibria in the reversible reaction of sulfur dioxide with oxygen, explain the effect of (*a*) high temperature, (*b*) high pressure, (*c*) increasing the partial pressure of oxygen, (*d*) the presence of a catalyst. Why does the industrial process operate at a temperature of approximately 400° and a pressure of one atmosphere?
8. Why is the sulfur trioxide produced in the converter by the contact process absorbed in concentrated sulfuric acid rather than in water?
9. Trace the flow of the gases in the lead chamber process, and indicate the part of the plant in which each reaction takes place.
10. What are the relative advantages of the two processes for the production of sulfuric acid?

11. Represent by equations four ionic reactions of sulfuric acid, which illustrate its acidic properties.
12. Represent by equations reactions of sulfuric acid due to sulfate ions. Describe the test for the presence of sulfate ions, and explain the function of hydrochloric acid in making this test.
13. Write equations for reactions of sulfuric acid due to its high boiling point. What application is made of this property?
14. Represent by equations, derived through the use of the ion-electron partial equations for the half reactions, the oxidation of the following substances by hot concentrated sulfuric acid: (a) copper; (b) mercurous sulfate; (c) a bromide; (d) an iodide.
15. Discuss the economic importance of sulfur, of sulfur dioxide, and of sulfuric acid. In connection with each of the uses, indicate the physical property or chemical reaction involved.

SUPPLEMENTARY READINGS

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chap. 1.

Furnas, C. C., *Rogers Manual of Industrial Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, chap. 7.

Badger, W. L., and E. M. Baker, *Inorganic Chemical Technology*, McGraw-Hill Book Company, Inc., New York, 1941, chap. III.

Fairlie, A. M., *Sulfuric Acid Manufacture*, Reinhold Publishing Corporation, New York, 1936.

Olsen, J. C., and H. Maisner, "Vanadium Catalysts," *Ind. Eng. Chem.* **29**, 255 (1937).

Jones, W. N., "Charles Goodyear," *Chem. Met. Eng.* **46**, 14 (1939).

Duecker, W. W., "Sulfur and National Defense," *Chem. Met. Eng.* **48**, 3, 71 (1941).

Johnstone, H. F., "Sulfur Dioxide," *Ind. Eng. Chem.* **34**, 1017 (1942).

"Sulfur Mining at Newgulf," Pictured Flow Sheet, *Chem. Met. Eng.* **48**, 3, 104 (1941).

"Contact Acid from Pyrites," Pictured Flow Sheet, *Chem. Met. Eng.* **46**, 8, 477 (1939).

Waitkins, G. R., A. E. Bearse, and R. Shutt, "Utilization of Selenium and Tellurium," *Ind. Eng. Chem.* **34**, 899 (1942).

Chapter 21

NITROGEN. AMMONIA. NITRIC ACID

Nitrogen is the element of lowest atomic number in Group V of the periodic system. The element has five valence electrons and forms compounds in a number of oxidation states. The lowest of its oxidation numbers is 3 −, and the highest 5 +. It also yields important compounds in the intermediate oxidation states 1 +, 2 +, 3 +, and 4 +. Nitrogen differs in many respects from the other elements in Group V. Ammonia, one of the hydrides of nitrogen, unlike the hydrides of the halogens and sulfur, is a base. Nitric acid is an important strong acid.

Occurrence of Nitrogen. Nitrogen occurs in the elementary condition in air and there are a number of natural compounds of this element, *e.g.*, ammonium salts, nitrates, and nitrites. About 75.4 per cent by weight of the atmosphere is nitrogen, but the element accounts for only approximately 0.03 per cent of the matter in the outer part of the earth. Nitrogen is a constituent of the proteins. Deposits of sodium nitrate are found in Chile, Turkestan, and Egypt. The most important of these deposits is in an arid region in Chile, and this salt is called *Chile saltpeter*. Complex nitrogen compounds are found in bituminous coal.

Preparation of Nitrogen. Nitrogen may be separated from the other atmospheric gases by liquefaction and fractionation. It has the lowest boiling point among the principal components of air. Nitrogen is also obtained from air by chemical processes in which oxygen, the other main component, is removed by reaction with other substances such as carbon or hydrogen. Nitrogen produced by these processes usually contains varying proportions of impurities. Pure nitrogen in limited quantities may be obtained by the decomposition of certain compounds. Ammonia is oxidized to nitrogen and water by passing it over hot cupric oxide.

$$2\,NH_3 + 3\,CuO \longrightarrow N_2 + 3\,H_2O + 3\,Cu$$
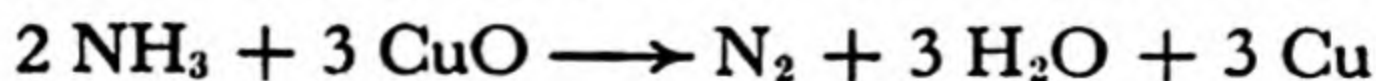
Ammonium nitrite is unstable toward heat, decomposing to yield nitrogen and water. Sodium nitrite and ammonium chloride are usually employed in this method of producing nitrogen, because of the instability of ammonium nitrite. Nitrogen is evolved when a solution of these substances is heated.

$$NH_4^+ + NO_2^- \longrightarrow N_2 + 2\,H_2O$$

Properties and Reactions of Nitrogen. Elementary nitrogen is a colorless and tasteless gas with no odor. It is slightly soluble in water. The critical temperature of nitrogen is $-146°$; the normal boiling point of the liquid, $-195.8°$; and the freezing point, $-210°$.

Molecules of nitrogen are diatomic and are very stable toward decomposition by heat and by chemical reactions. Hence, the element has low activity. Nitrogen becomes activated when it is subjected to the action of a high voltage discharge, *i.e.*, electrons at high velocity. In this condition it combines with many elements with which it does not ordinarily react. It is assumed that this active form of nitrogen is atomic in composition and that some of its valence electrons are at a higher energy level than normal.

Nitrogen reacts with several substances at high temperatures. It unites with magnesium and aluminum and a few of the other metals, producing nitrides.

$$3\,Mg + N_2 \longrightarrow Mg_3N_2$$
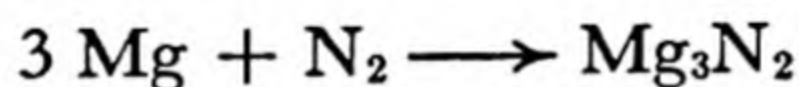
Nitrogen and oxygen react at the temperature of the electric arc to form nitric oxide. The reaction is reversible, and the percentage of the oxide at equilibrium is small.

$$N_2 + O_2 \rightleftharpoons 2\,NO$$
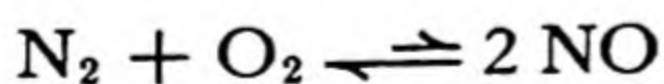
The most important reaction of the element is with hydrogen, at high pressures and moderately high temperatures, to form ammonia.

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$
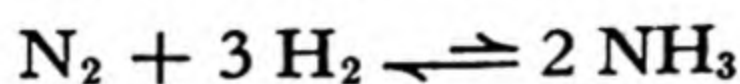
Nitrogen reacts with calcium carbide at a temperature of approximately 1000°, producing calcium cyanamide and carbon.

$$N_2 + CaC_2 \longrightarrow CaNCN + C$$
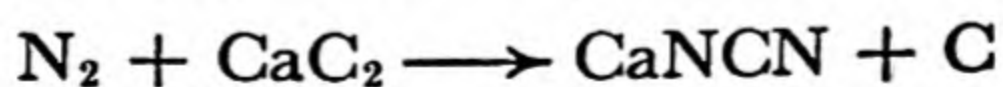
Sodium cyanide may be formed by heating a mixture of sodium

carbonate and carbon, containing iron as a catalyst, in a current of nitrogen.

$$Na_2CO_3 + 4\,C + N_2 \longrightarrow 2\,NaCN + 3\,CO$$
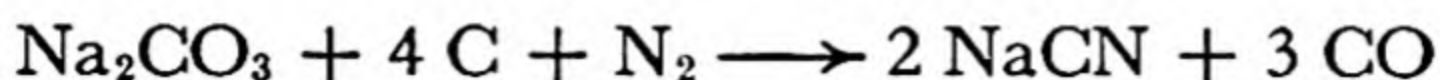
Nitrides of Metals. The metals that unite directly with nitrogen to form nitrides also react with ammonia when heated in an atmosphere of this gas.

$$3\,Mg + 2\,NH_3 \longrightarrow Mg_3N_2 + 3\,H_2$$

The metal nitrides are decomposed by water with the formation of the metal hydroxide and ammonia.

$$Mg_3N_2 + 6\,H_2O \longrightarrow 3\,Mg(OH)_2\!\downarrow + 2\,NH_3$$
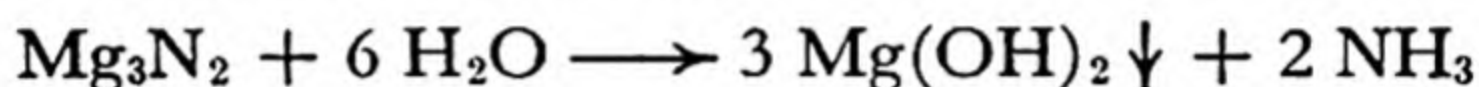
The hydrolysis of magnesium nitride is an irreversible process, since both products are basic, and neither hydronium nor hydroxide ions may remain in contact with the nitride in the concentrations required for equilibrium with molecular water.

Halides of Nitrogen. Nitrogen trichloride is formed by the reaction of an excess of chlorine with ammonium chloride in strongly acidic solution.

$$NH_4{}^+ + 3\,Cl_2 \longrightarrow NCl_3 + 4\,H^+ + 3\,Cl^-$$
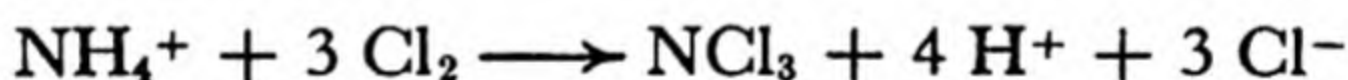
This compound is a violently explosive, yellow, oily liquid. It is partially hydrolyzed with the formation of ammonia and hypochlorous acid. Nitrogen triiodide is formed by the reaction of iodine with a solution of ammonia.

$$4\,NH_3 + 3\,I_2 \longrightarrow NI_3 + 3\,NH_4{}^+ + 3\,I^-$$

This substance precipitates as a brown solid, having the composition $NI_3(NH_3)$. It may be handled safely while it is moist, but decomposes at slight shock when dry.

Importance of Nitrogen and Nitrogen Compounds. Elementary nitrogen has few direct uses of importance. It is used in gas-filled electric light bulbs with tungsten filaments to decrease the rate at which the filament evaporates. The stems of mercury thermometers may be filled with nitrogen under pressure to raise the boiling temperature of the mercury and make possible the use of such thermometers at temperatures somewhat above the normal boiling point of mercury, 356.9°. Nitrogen compounds are of fundamental importance in modern civilization. The harvesting of

agricultural products containing nitrogenous substances removes them from the soil where they grew and upsets the balance between the amount of these compounds taken out of the soil and the amount returned to it by natural agencies, such as bacterial action, the decay of organic matter, and the combination of nitrogen and oxygen at the temperature of the electric discharge in thunderstorms. Hence, fertilizers containing soluble nitrogen compounds must be applied in order to maintain the fertility of the soil. Ammonium sulfate and sodium nitrate are the compounds employed most widely as chemical fertilizers. Ammonia is used extensively as a refrigerant. Nitric acid is essential to the manufacture of high explosives and of a large number of dyes, drugs, and other commercial products.

Sources of Nitrogen Compounds. There are three important industrial sources of nitrogen compounds. The deposits of sodium nitrate in Chile contain a large quantity of this salt, but transportation problems must be overcome to make it available in other countries. The destructive distillation of coal yields nitrogen compounds, chiefly ammonia, among the volatile products. Atmospheric nitrogen is now the most important source of nitrogen compounds. Accurate figures for the total production of nitrogen compounds in recent years are not available, but it is known that the production of synthetic ammonia is great enough to meet all requirements. The requirements for agricultural use in the continental United States during 1943 were approximately 460,000 tons of combined nitrogen. A large proportion of the supply must come from atmospheric nitrogen.

The Fixation of Nitrogen. The production of nitrogen compounds from atmospheric nitrogen is called *nitrogen fixation*. At present, only two of the reactions of elementary nitrogen mentioned in a preceding paragraph are important for the industrial production of nitrogen compounds. The reaction of nitrogen with hydrogen is employed in the synthetic ammonia processes, and the reaction with calcium carbide in the cyanamide process.

Direct Synthetic Processes. The formation of ammonia by the union of nitrogen and hydrogen was discovered in the latter part of the nineteenth century, but the industrial application of the reaction was not made until 1913, because the yield was too small

for a practicable process. The equilibria involved in the system were investigated by Haber, Nernst, and others, particularly in Germany, and favorable conditions were found for increasing the yield. The combination of the elements is a reversible reaction with a low velocity even at fairly high temperatures. The formation of ammonia is exothermic.

$$N_2 + 3 H_2 \rightleftharpoons 2 NH_3 + 24,400 \text{ cal.}$$
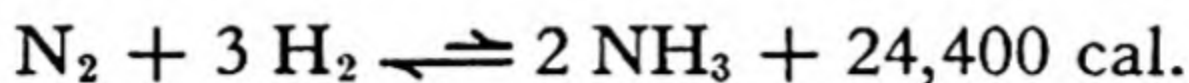
Consequently, the proportions of ammonia in the equilibrium mixture decrease as the temperature is raised to increase the velocity of reaction. The percentage of ammonia in equilibrium mixtures at various temperatures is shown in Fig. 95. At a pressure of 100 at-
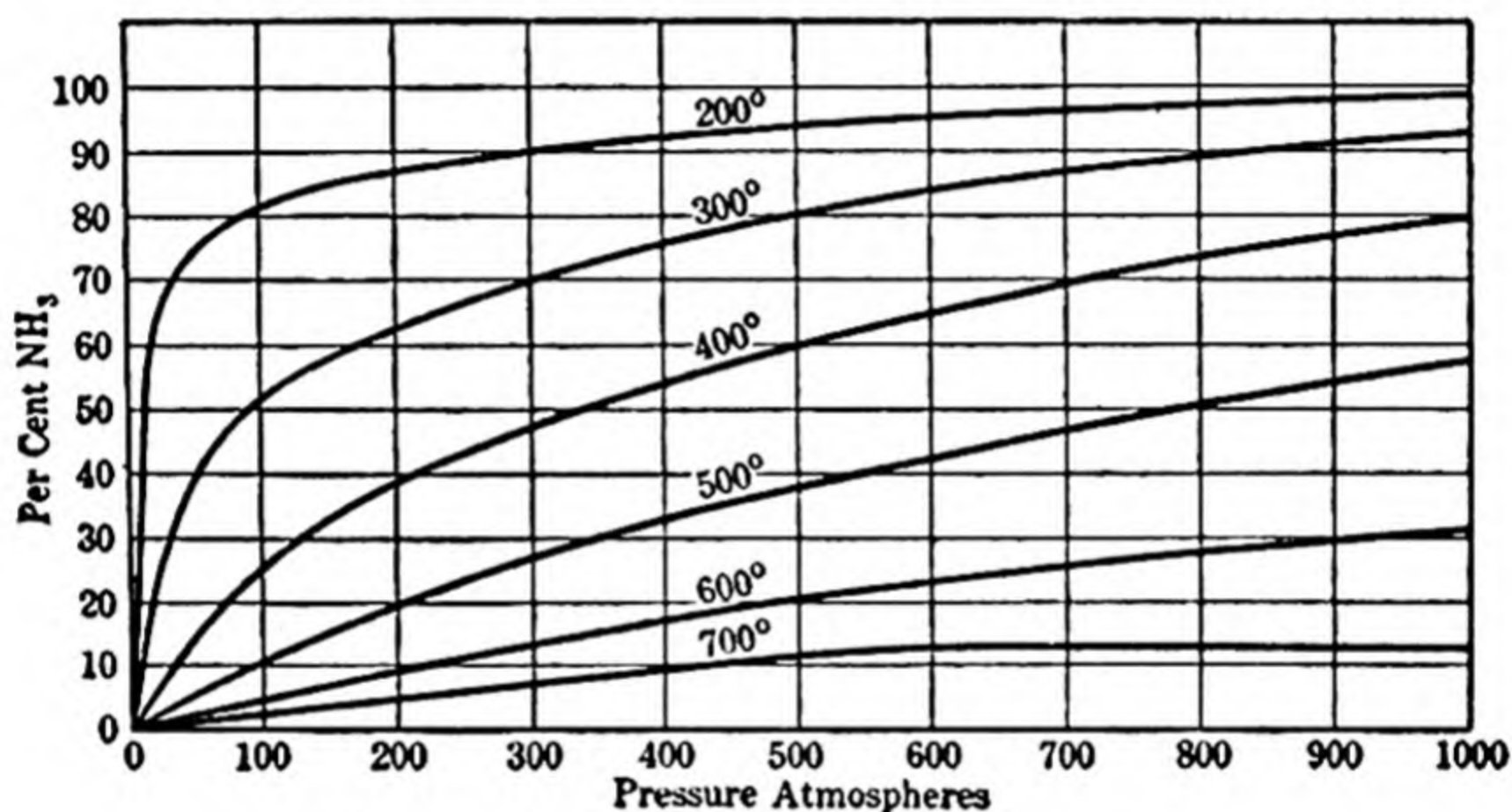
Fig. 95. Equilibrium Yield of Ammonia

mospheres, the per cent of ammonia is approximately 80 in the equilibrium mixture at 200°, and 10, at 500°. Evidently, the process must be operated at the lowest temperature giving sufficient reaction velocity to make it practical.

The volume ratio in which the elementary gases react is four of the initial gases to two of product. Hence, in accord with Le Chatelier's principle, the proportion of ammonia in the equilibrium mixture becomes greater as the pressure is increased. This effect is shown in Fig. 95. Two factors contribute to this effect, viz., the normal concentration effect and additional effects due to molecular attraction at high pressures. The molecular forces of attraction are greater for ammonia, a gas with relatively high critical temperature, than for nitrogen and hydrogen, which have

low critical temperatures, and the equilibrium constant is greater at high than low pressures.

$$\frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = K$$

At 450°, the equilibrium constant is 0.00659 at a pressure of 10 atmospheres; 0.00725 at 100 atmospheres; and 0.02328 at 1000 atmospheres.

The reaction proceeds too slowly in the absence of a catalyst to be of practical importance, even at high temperatures and pressures. A number of contact catalysts accelerate this reaction, but the most effective catalysts consist of very porous iron, containing small percentages of "promoters," one strongly basic, as potassium oxide, and the other weakly acidic, as aluminum oxide.

The Haber process, operating at 500° and 200 atmospheres, began production at Oppau in Germany in 1913. Some processes are now operated at 450° and others at temperatures as high as 600°. The pressure likewise varies in different processes from 100 atmospheres to 1000 atmospheres. The ammonia formed during the passage of the gases through the catalyst is separated from the gas mixture by refrigeration, and the uncombined gases are recirculated. The equilibrium yield of ammonia depends on the temperature and pressure, but the practical yield depends also on the purity of the gases, the activity of the catalyst, and the rate of gas flow through the catalytic material. The actual yield is much less than the percentage of ammonia in the equilibrium mixture, because it is not economical to hold the gases in contact with the catalyst long enough to attain equilibrium.

The Cyanamide Process. The reaction of nitrogen with calcium carbide produces calcium cyanamide, CaNCN. This reaction was discovered in 1895 by the German chemists, Caro and Frank. Commercial production of calcium cyanamide was begun in Germany in 1906. Calcium carbide is produced by heating a mixture of lime and coke in an electric furnace at a temperature of approximately 3000°.

$$CaO + 3 C \longrightarrow CaC_2 + CO$$
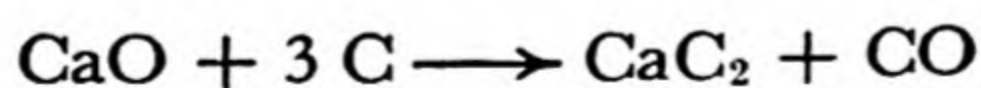
The molten carbide is withdrawn from the furnace, cooled, and

pulverized. Nitrogen from liquid air is then passed over the calcium carbide at a temperature of approximately 1100°.

$$CaC_2 + N_2 \longrightarrow CaNCN + C + 98,430 \text{ cal.}$$

Since the reaction is highly exothermic, it is necessary to heat only a portion of the charge to start the reaction.

Ammonia may be produced from calcium cyanamide by reaction with steam under a pressure of 3–4 atmospheres.

$$CaNCN + 3 H_2O \longrightarrow CaCO_3 + 2 NH_3$$

Nevertheless, the chief source of ammonia is the direct synthetic process. The cyanamide process is important primarily for the production of cyanides, urea, and many other organic nitrogen compounds.

AMMONIA

Ammonia is the most important hydride of nitrogen. It is the product of the direct synthetic processes for the fixation of nitrogen. The annual production of ammonia in the United States now amounts to several hundred thousand tons. A large proportion of the ammonia is converted into other compounds of nitrogen.

Production of Ammonia from Coal. Bituminous coal contains small percentages of nitrogen, 1–2.5 per cent, in the form of complex compounds. These compounds decompose during the destructive distillation of coal, and approximately one half of the nitrogen is evolved as ammonia. Ammonia is separated from the other gaseous products by absorption in dilute sulfuric acid to form ammonium sulfate.

$$NH_3 + H^+ \longrightarrow NH_4^+$$
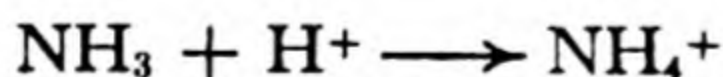
Ammonium sulfate is used as a plant fertilizer and as a source of ammonia gas.

Preparation of Ammonia from Ammonium Sulfate. Ammonia is produced from ammonium salts by reaction with strong bases. Ammonium sulfate and calcium hydroxide are commonly selected, but other ammonium salts and other bases may be used. Ammonia gas is evolved when a mixture of the solids is heated.

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2 NH_3 \uparrow + 2 H_2O$$
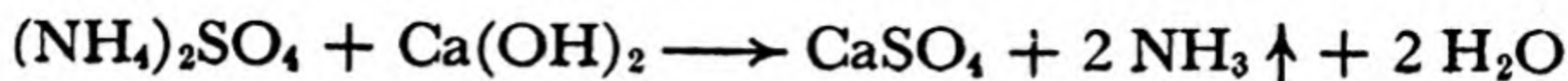
A convenient method for laboratory preparation of ammonia is based on this reaction. A sketch of the apparatus (Fig. 96) indicates the collection of the gas by the downward displacement of air. This method is used because ammonia is soluble in water and is less dense than air.
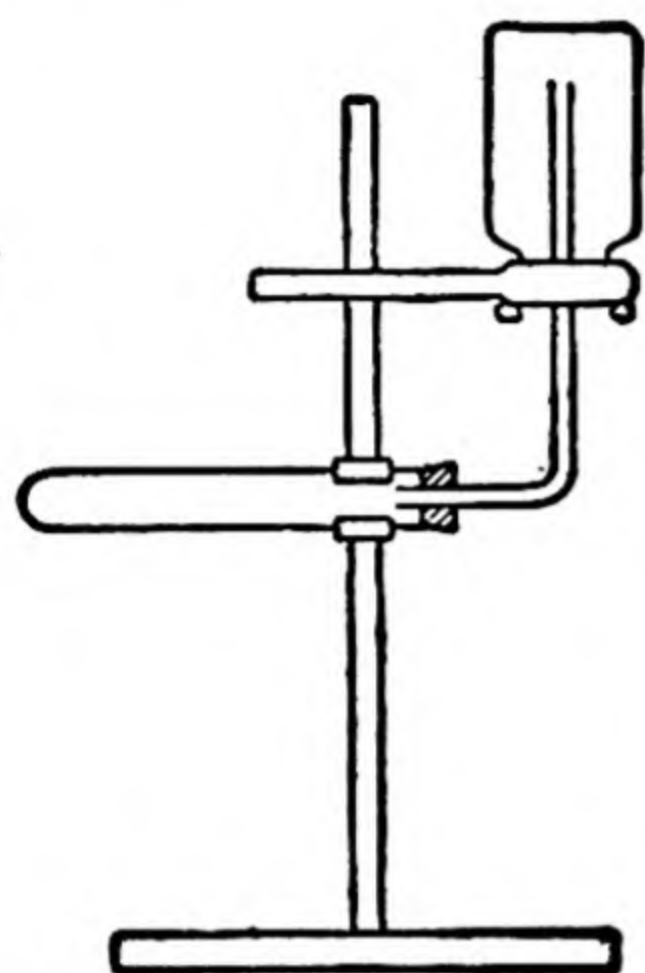
Fig. 96. *Apparatus for Laboratory Preparation of Ammonia*

Properties of Ammonia. Ammonia is a colorless gas that causes suffocation when inhaled in too great concentration. The saturated solution at a temperature of 18° and a gas pressure of one atmosphere contains 36 per cent of ammonia. The critical temperature of ammonia is 133°, and the gas may be easily liquefied by pressure at room temperature. Liquid ammonia boils at $-33.5°$ and has a vapor pressure of 4.2 atmospheres at 0°. The freezing point of the substance is $-77.7°$.

Reactions of Ammonia. Ammonia is a molecular base which takes up protons to form ammonium ions. It yields a weakly basic solution with water.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = K = 1.8 \times 10^{-5}$$
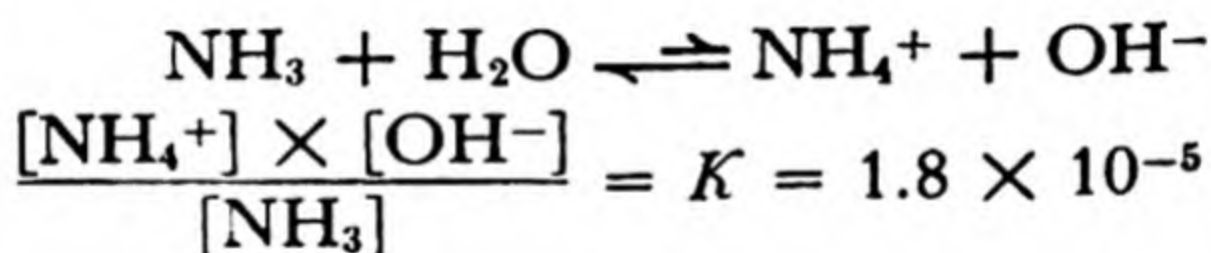
The addition of an ammonium salt decreases the concentration of the hydroxide ions, giving a weakly basic solution containing a regulated concentration of hydroxide ions. Ammonia reacts with acids to form ammonium salts. The ammonium salts of the strong acids are acidic in solution, because of the hydrolysis of the ammonium ion.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$
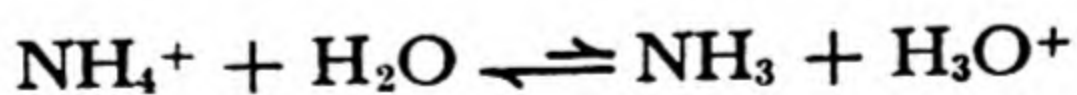
The formation of a white smoke by reaction with gaseous hydrogen chloride and the odor of the gas serve as tests for the presence of ammonia.

Although ammonia does not exhibit acidity in solution, the gas does react with some of the active metals with the formation of free hydrogen. In the reaction of ammonia with sodium, one

third of the hydrogen is displaced, producing a compound known as *sodamide*, $NaNH_2$.

$$2 NH_3 + 2 Na \longrightarrow 2 NaNH_2 + H_2$$
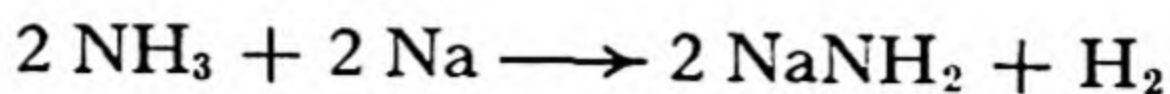
Potassium reacts in a similar manner, but calcium yields the nitride.

$$3 Ca + 2 NH_3 \longrightarrow Ca_3N_2 + 3 H_2$$
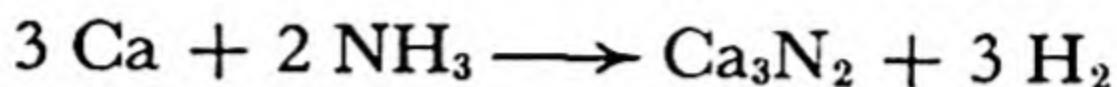
Ammonia adds directly to a number of metal ions with the formation of complex ions. This property is attributed to the unshared pair of electrons in the ammonia molecule, which form coordinate bonds with the metal ions involved.

$$Cu^{++} + 4 NH_3 \rightleftharpoons Cu(NH_3)_4^{++}$$
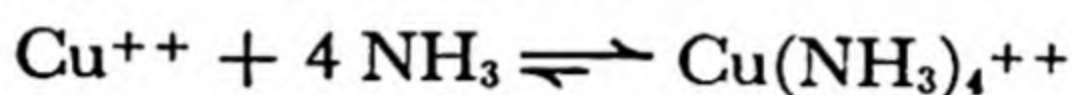
Ammonia is unstable toward heat and is almost entirely decomposed into the elements at temperatures above 700°.

$$2 NH_3 \rightleftharpoons N_2 + 3 H_2$$
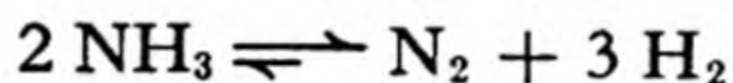
Gaseous ammonia reacts with hot copper oxide to form free nitrogen, copper, and water, as discussed above. Ammonia burns in oxygen, forming nitrogen and water.

$$4 NH_3 + 3 O_2 \longrightarrow 2 N_2 + 6 H_2O$$
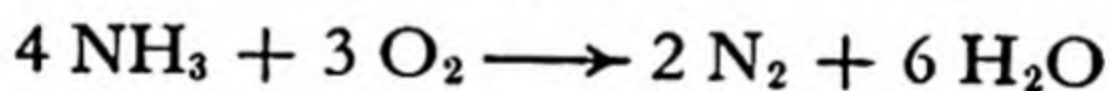
Ammonia is selectively oxidized to nitric oxide and water at higher temperature in the presence of platinum as a catalyst.

$$4 NH_3 + 5 O_2 \longrightarrow 4 NO + 6 H_2O$$
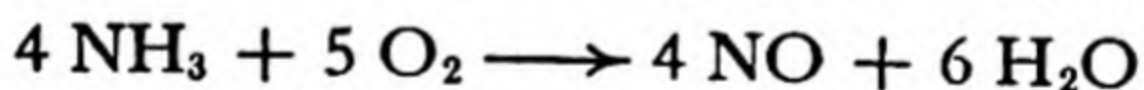
The industrial method for the conversion of ammonia into nitric acid employs this reaction as the first step.

Uses of Ammonia. Ammonia is extensively used in refrigeration because it is easily liquefied by pressure at ordinary temperatures and possesses a high heat of vaporization. Liquid ammonia is allowed to drop through an expansion valve into a coil of pipe surrounded by a solution of calcium chloride. The evaporation of ammonia cools the brine to a temperature far below the freezing point of water. Pure water, contained in tanks suspended in the brine, freezes. The brine itself is circulated in pipes through the chambers of cold storage plants.

Ammonia is now used on a large scale in the formation of nitric oxide for the production of nitric acid and of sulfuric acid by the lead chamber process. It is employed also in the production of

sodium carbonate by the Solvay process and in the preparation of ammonium salts and of household ammonia solutions for use as a cleansing agent.

NITRIC ACID

There are several oxyacids of nitrogen, the most important being nitric acid. These acids are easily reduced with the formation of products containing nitrogen in lower states of oxidation. Even in dilute solution, the oxidizing properties of the oxyacids of nitrogen are prominent.

Nitric acid has great industrial importance. More than one half of the annual production is used in the formation of nitro compounds and of nitrates containing organic radicals. Some of these compounds are high explosives, others are important in the production of plastics and synthetic drugs and dyes. The nitrates of the metals have important applications, notably the use of sodium nitrate in mixed fertilizers.

Production of Nitric Acid from Ammonia. A large proportion of the nitric acid produced in the United States is obtained from ammonia. The process involves three essential reactions, *viz.*, the oxidation of ammonia to form nitric oxide, the combination of nitric oxide with oxygen to form nitrogen dioxide, and the reaction of the dioxide with water forming nitric acid. Ammonia may be oxidized to form both free nitrogen and nitric oxide. In contact with a platinum gauze catalyst, the velocity of the reaction producing nitric oxide is accelerated so greatly that a 95 per cent conversion may be secured. A mixture of ammonia and air containing approximately 10 per cent of ammonia is passed over platinum gauze at a temperature of about 1000°. The gases are preheated to about 300°, and the heat of the reaction is sufficient to maintain the high temperature required.

$$4 NH_3 + 5 O_2 \longrightarrow 4 NO + 6 H_2O$$
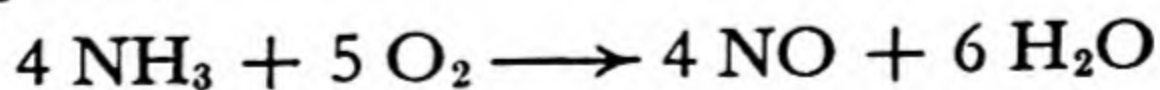
The gases then pass into absorption towers constructed of acid resistant materials such as chrome steel. The gases are cooled in the towers and further reactions take place.

The reaction of nitric oxide with oxygen is exothermic and is reversible at temperatures between 150° and 620°.

$$2 NO + O_2 \rightleftharpoons 2 NO_2 + 27,800 \text{ cal.}$$
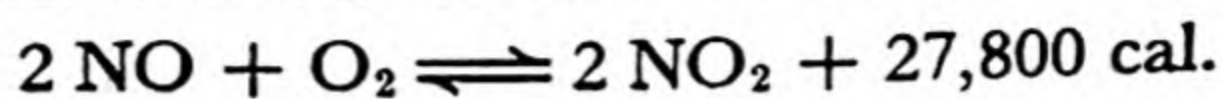
Conversion into the dioxide is complete at temperatures below 150°. Nitrogen dioxide reacts with warm water to form nitric acid and nitric oxide as the principal products.

$$3 NO_2 + H_2O \longrightarrow 2 H^+ + 2 NO_3^- + NO$$
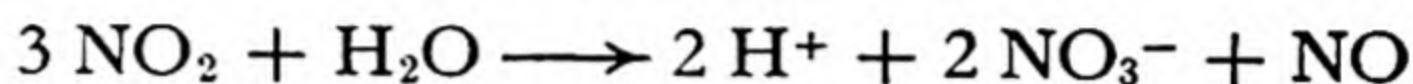
The nitric oxide liberated in this reaction is again oxidized by the excess of oxygen in the gas mixture. Nearly complete conversion of the oxide into nitric acid may be accomplished by regulating the rate of gas flow. A mixture of nitric and nitrous acids is produced with low concentrations of nitrogen dioxide and cold water.

$$2 NO_2 + H_2O \rightleftharpoons H^+ + NO_3^- + HNO_2$$
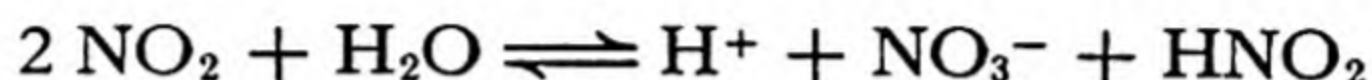
A mixture of the nitrate and nitrite is formed by the use of a solution of sodium carbonate in the final absorption tower, and the reaction is completed by the neutralization of the acids.

$$CO_3^{--} + H^+ + HNO_2 \longrightarrow NO_2^- + CO_2 + H_2O$$

Production of Nitric Acid from Sodium Nitrate. Nitric acid may be prepared by the reaction of concentrated sulfuric acid with sodium nitrate. This reaction was formerly the principal source of nitric acid, but it now yields only a small percentage of the total production. In the laboratory method, a mixture of sodium nitrate and concentrated sulfuric acid is

Fig. 97. Laboratory Apparatus for the Preparation of Nitric Acid

heated in a glass retort. (Fig. 97.) Nitric acid is boiled out of the mixture and is condensed.

$$NaNO_3 + H_2SO_4 \longrightarrow HNO_3 + NaHSO_4$$
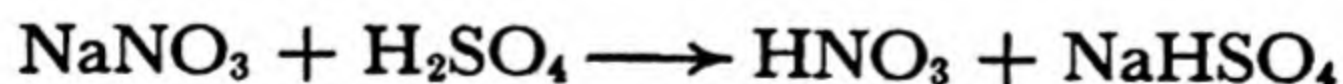
In the industrial method, the mixture is heated in large iron retorts and the acid is condensed in tubes made of glass or acid resistant iron alloys such as duriron which contains 16 per cent of silicon.

Nitric acid may be distilled from the mixture at lower temperatures if reduced pressures are employed, and the percentage that decomposes is reduced in this manner. Sodium hydrogen sulfate reacts with sodium nitrate at higher temperatures, but the second stage of the reaction is not important because too much of the acid is decomposed at the higher temperature.

Properties of Nitric Acid. Pure nitric acid is a colorless liquid with a normal boiling point of 86°. It is soluble in water in all proportions. The abnormally great vapor pressure effects in these solutions are due to reaction between the solute and the solvent. The solution containing 68 per cent of the acid has a specific gravity of 1.41 and boils at 120.5° without change in composition. (See page 123.) Usually, the concentrated laboratory reagent has a concentration of approximately 15 M. Concentrated solutions of nitric acid are frequently yellow or brown because of the presence of nitrogen dioxide in solution. This product is formed by the slow decomposition of the acid.

Reactions of Nitric Acid. The anhydrous substance is unstable toward heat and partially decomposes while being distilled under atmospheric pressure.

$$4\,HNO_3 \longrightarrow 2\,H_2O + 4\,NO_2 + O_2$$
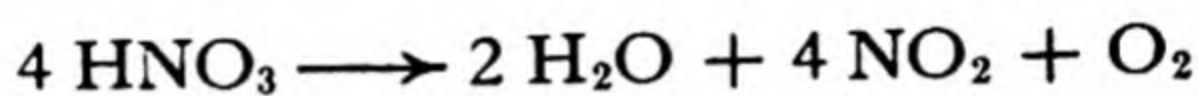
The acid may be dehydrated by the action of phosphorus pentoxide yielding *nitrogen pentoxide*, N_2O_5.

$$2\,HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2\,HPO_3$$
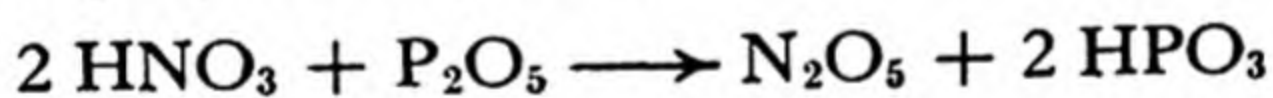
This reaction occurs at low temperatures, and the hydration product of phosphorus pentoxide under these conditions is metaphosphoric acid, HPO_3. Nitrogen pentoxide is a white solid which melts at 30° and boils at 47°. The vapor pressure of the solid is high, and it sublimes unless a high pressure of the vapor is maintained.

Nitric acid has a number of important reactions. These may be classified into four important types, *viz.*, general acid reactions, esterification, nitration, and oxidation-reduction.

Acid Reactions of Nitric Acid. The anhydrous substance is a molecular acid that ionizes in aqueous solution to form hydrogen and nitrate ions.

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$
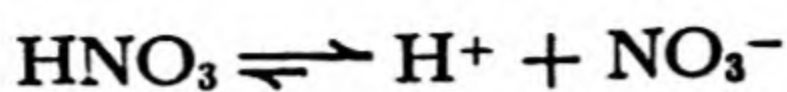
Nitric acid is a strong acid that reacts vigorously with the different classes of basic substances, *viz.*, metal hydroxides, metal oxides, ammonia, and the anions of weak acids. Nitric acid also reacts with most of the metals, but hydrogen is not the usual reduction product.

Esterification with Nitric Acid. Nitric acid reacts with a number of the alcohols, forming products known as esters. The alcohols are compounds of carbon, hydrogen, and oxygen, containing the hydroxide group. During the reaction of esterification, an atom of hydrogen from the hydroxide group of the alcohol and two atoms, one of hydrogen and one of oxygen, from the acid are removed with the formation of water. The residues of the two molecules add together to form the ester. A mixture of concentrated nitric and sulfuric acids is commonly used in this reaction, sulfuric acid serving as a dehydrating agent. Glycerol, an alcohol containing three hydroxide groups per molecule, reacts with a mixture of concentrated nitric and sulfuric acids with the formation of *glyceryl trinitrate*, commonly called *nitroglycerine*.

$$C_3H_5(OH)_3 + 3\ HONO_2 \longrightarrow C_3H_5(ONO_2)_3 + 3\ H_2O$$

In a similar reaction, cellulose yields the trinitrate, called *trinitrocellulose* or *guncotton*. These substances are high explosives. *High explosives* are substances in which the explosion reaction is transmitted practically instantaneously throughout the entire charge. This is known as detonation. Other esters of cellulose, containing smaller proportions of the nitrate radical than guncotton, are used in the production of celluloid, collodion, and other plastic materials. The mixture of these lower nitrate esters is known as *pyroxylin*.

Nitration. Concentrated nitric acid reacts with some of the hydrocarbons and certain other substances known as hydrocarbon derivatives because of structural similarities. The products of this reaction are known as *nitro compounds*. They are formed by the substitution of an atom of hydrogen in the complex molecule by the nitro group, $-NO_2$. This reaction is called *nitration*. Benzene reacts with nitric acid forming nitrobenzene.

$$C_6H_6 + HONO_2 \longrightarrow C_6H_5NO_2 + H_2O$$
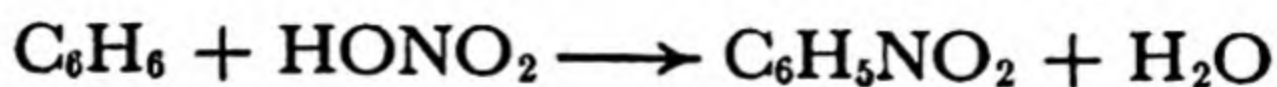
Concentrated sulfuric acid is also commonly used in this reaction as a dehydrating agent. Under these conditions, three nitro groups may be introduced into the benzene molecule, replacing three atoms of hydrogen. The product is trinitrobenzene.

$$C_6H_6 + 3\ HONO_2 \longrightarrow C_6H_5(NO_2)_3 + 3\ H_2O$$
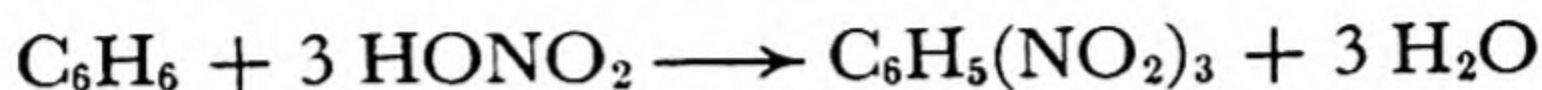
The most extensive use of nitric acid is in the nitration reaction. Several of the nitro compounds are high explosives, *e.g.*, trinitrotoluene, T. N. T., and trinitrophenol, picric acid. A number of nitro compounds are valuable intermediates for use in the production of dyes, drugs, lacquers, and plastics.

Oxidizing Action of Nitric Acid. The oxidation number of nitrogen in nitric acid is 5 +, and the element yields compounds in several lower states of oxidation. The decomposition of the nitrate ion to form these products requires a gain of electrons, and nitric acid is an active oxidizing agent. The following ion-electron equations represent the half reactions involved in the formation of some of the more common reduction products. The standard oxidation-reduction potentials (see page 299) at 25° are listed for each of these half reactions.

$$2\ H^+ + NO_3^- + 1\ \epsilon \longrightarrow NO_2 + H_2O \ldots + 0.81 \text{ volt}$$
$$4\ H^+ + NO_3^- + 3\ \epsilon \longrightarrow NO + 2\ H_2O \ldots + 0.96 \text{ volt}$$
$$10\ H^+ + NO_3^- + 8\ \epsilon \longrightarrow NH_4 + 3\ H_2O \ldots + 0.87 \text{ volt}$$
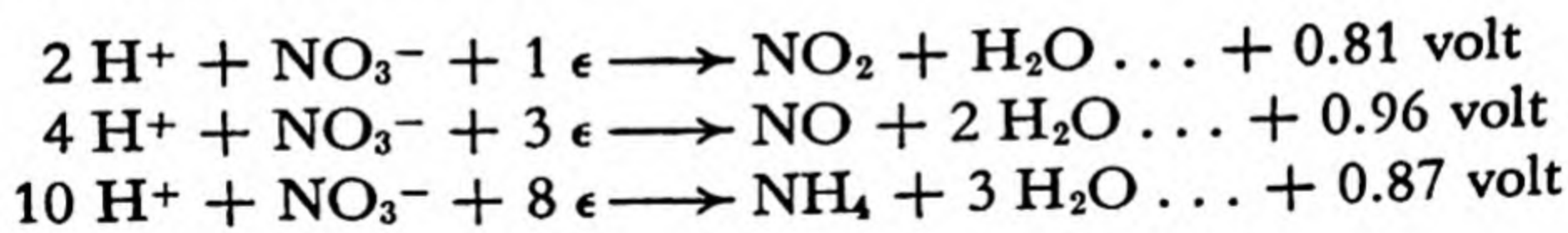
These figures are the potentials for one molal concentration. The oxidizing activity is much greater in higher concentrations. Still other reduction products may be formed, and a mixture of products is usually obtained. The principal product in any one of these reactions depends on the concentration of the acid, the temperature, the activity of the reducing agent, and the relative rates of the various reactions. Concentrated nitric acid of about 1.4 specific gravity yields nitrogen dioxide as the principal product, but the moderately concentrated acid of 1.2 specific gravity yields almost pure nitric oxide. Generally, the moderately concentrated acid is used, and the common reduction product is nitric oxide.

The nature of the oxidation products, as considered previously on page 302, depends on the nature of the reducing agents. In the following examples, the equations will be shown for the reaction

of the moderately concentrated acid. Nitric acid reacts with metallic silver to produce a solution of silver nitrate.

$$4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O$$
$$\underline{[Ag \longrightarrow Ag^+ + 1\,\epsilon] \times 3}$$
$$4\,H^+ + NO_3^- + 3\,Ag \longrightarrow NO + 3\,Ag^+ + 2\,H_2O$$
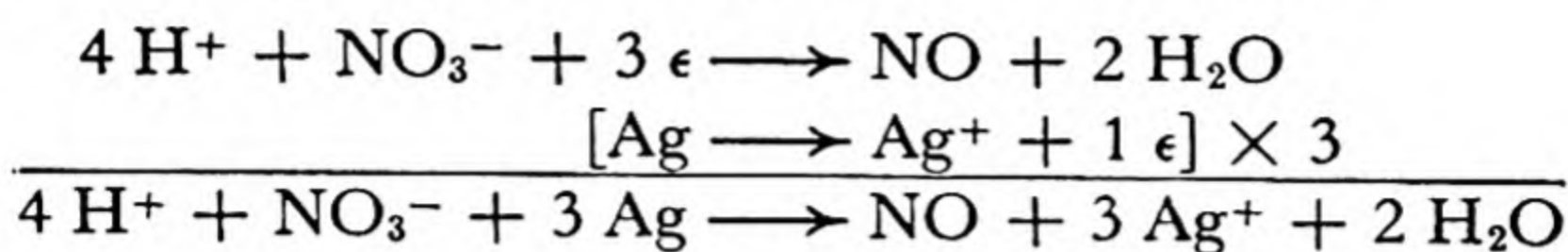
Mercurous nitrate is oxidized to form mercuric nitrate.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 2$$
$$\underline{[Hg_2^{++} \longrightarrow 2\,Hg^{++} + 2\,\epsilon] \times 3}$$
$$8\,H^+ + 2\,NO_3^- + 3\,Hg_2^{++} \longrightarrow 2\,NO + 6\,Hg^{++} + 4\,H_2O$$
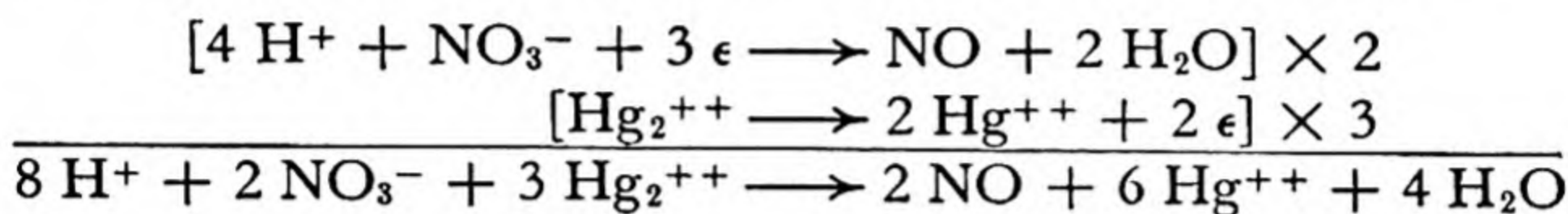
The slightly soluble cupric sulfide is oxidized to form free sulfur and a solution of cupric nitrate.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 2$$
$$\underline{[CuS \longrightarrow S + Cu^{++} + 2\,\epsilon] \times 3}$$
$$8\,H^+ + 2\,NO_3^- + 3\,CuS \longrightarrow 2\,NO + 3\,S + 3\,Cu^{++} + 4\,H_2O$$
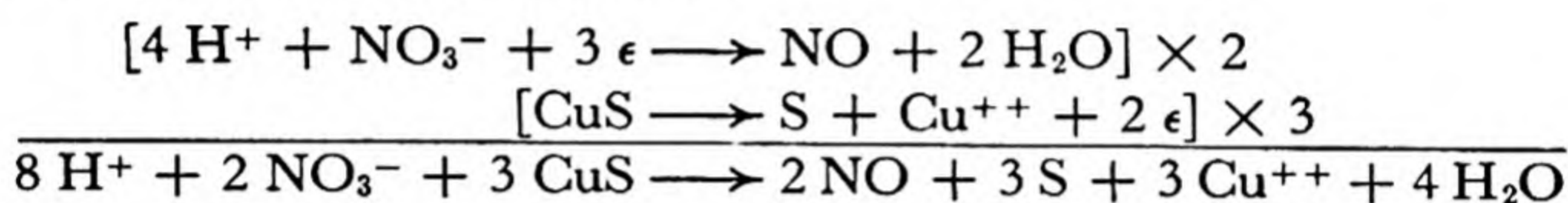
The elementary nonmetal, arsenic, yields weakly ionized arsenic acid when it is oxidized by nitric acid.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 5$$
$$\underline{[As + 4\,H_2O \longrightarrow H_3AsO_4 + 5\,H^+ + 5\,\epsilon] \times 3}$$
$$5\,H^+ + 5\,NO_3^- + 3\,As + 2\,H_2O \longrightarrow 5\,NO + 3\,H_3AsO_4$$
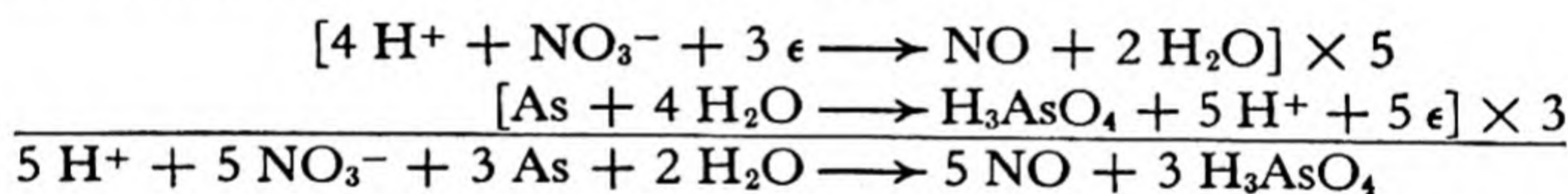
Sulfur dioxide in solution, or sulfurous acid, is oxidized to sulfuric acid.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 2$$
$$\underline{[SO_2 + 2\,H_2O \longrightarrow SO_4^{--} + 4\,H^+ + 2\,\epsilon] \times 3}$$
$$2\,NO_3^- + 3\,SO_2 + 2\,H_2O \longrightarrow 2\,NO + 3\,SO_4^{--} + 4\,H^+$$
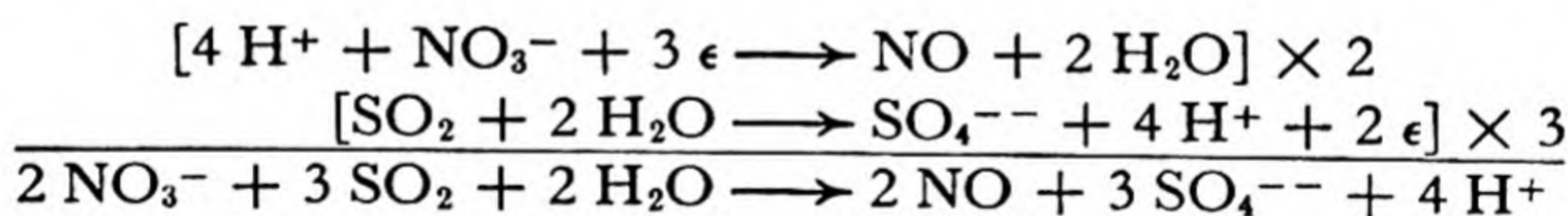
Hot concentrated nitric acid is frequently employed for reactions in which the activity of the reducing agent is low. Under these conditions, nitrogen dioxide is the principal reduction product. Arsenic trisulfide may be oxidized by hot concentrated nitric acid, producing sulfuric and arsenic acids.

$$[2\,H^+ + NO_3^- + 1\,\epsilon \longrightarrow NO_2 + H_2O] \times 28$$
$$\underline{As_2S_3 + 20\,H_2O \longrightarrow 2\,H_3AsO_4 + 3\,SO_4^{--} + 34\,H^+ + 28\,\epsilon}$$
$$22\,H^+ + 28\,NO_3^- + As_2S_3 \longrightarrow 28\,NO_2 + 2\,H_3AsO_4 + 3\,SO_4^{--} + 8\,H_2O$$
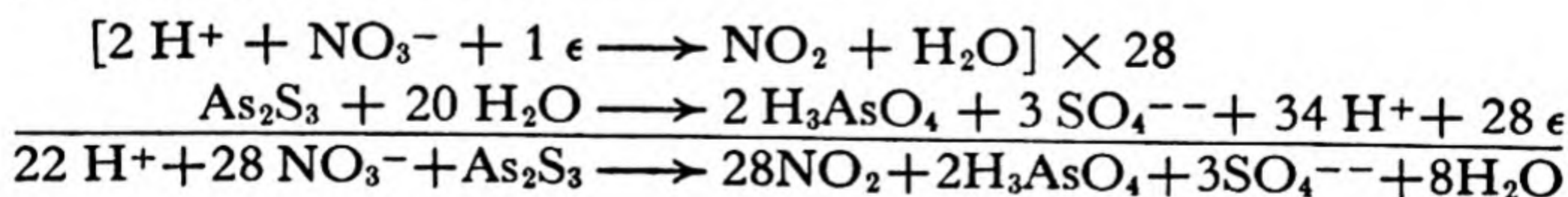
Dilute nitric acid, approximately 1 M., reacts with active reducing agents forming ammonium ions among the reduction products.

$$10\,H^+ + NO_3^- + 8\,\epsilon \longrightarrow NH_4^+ + 3\,H_2O$$
$$[Zn \longrightarrow Zn^{++} + 2\,\epsilon] \times 4$$
$$\overline{10\,H^+ + NO_3^- + 4\,Zn \longrightarrow NH_4^+ + 4\,Zn^{++} + 3\,H_2O}$$
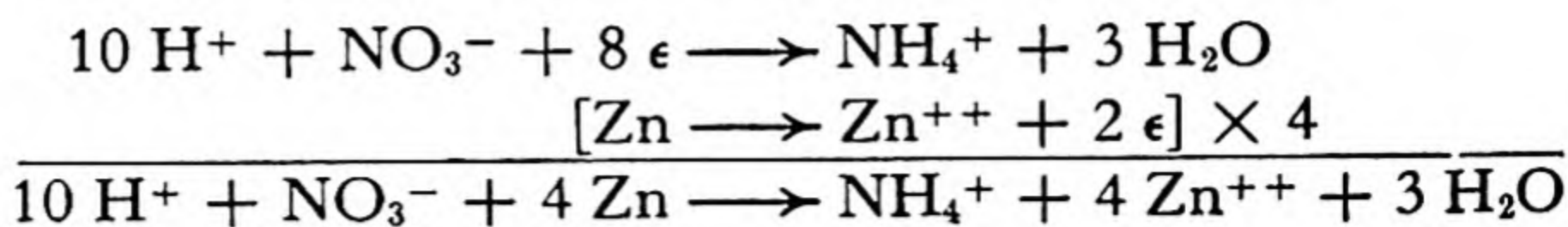
Aqua Regia. Nitric acid reacts with chloride ions to form *nitrosyl chloride*, NOCl, and free chlorine.

$$4\,H^+ + NO_3^- + Cl^- + 2\,\epsilon \longrightarrow NOCl + 2\,H_2O$$
$$2\,Cl^- \longrightarrow Cl_2 + 2\,\epsilon$$
$$\overline{4\,H^+ + NO_3^- + 3\,Cl^- \longrightarrow NOCl + Cl_2 + 2\,H_2O}$$
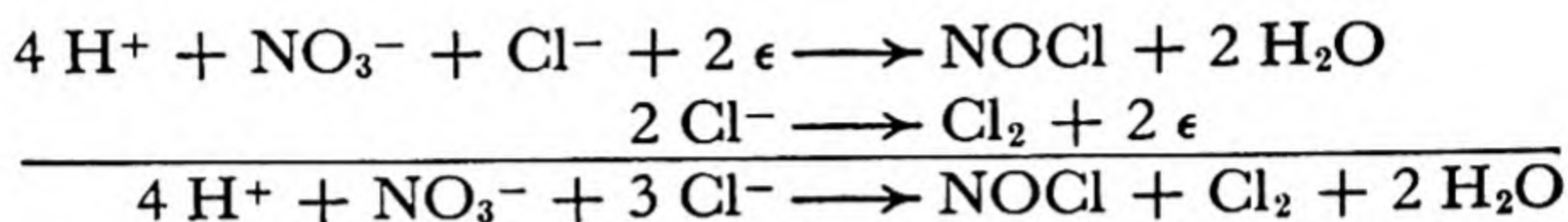
Nitrosyl chloride is a liquid with a normal boiling point of $-5.6°$. It rapidly decomposes into nitric oxide and chlorine when heated.

$$2\,NOCl \longrightarrow 2\,NO + Cl_2$$
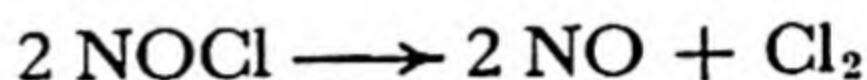
A mixture of concentrated nitric and hydrochloric acids, in a volume ratio of one to three, dissolves platinum which is inactive toward either acid alone. The acid mixture is called *aqua regia*. The reaction is due to the increased reducing activity of platinum in the presence of chloride ions, not to an increased oxidizing activity. The product is the complex *chloroplatinic acid*, H_2PtCl_6.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 4$$
$$[Pt + 2\,H^+ + 6\,Cl^- \longrightarrow H_2PtCl_6 + 4\,\epsilon] \times 3$$
$$\overline{22\,H^+ + 4\,NO_3^- + 3\,Pt + 18\,Cl^- \longrightarrow 4\,NO + 3\,H_2PtCl_6 + 8\,H_2O}$$
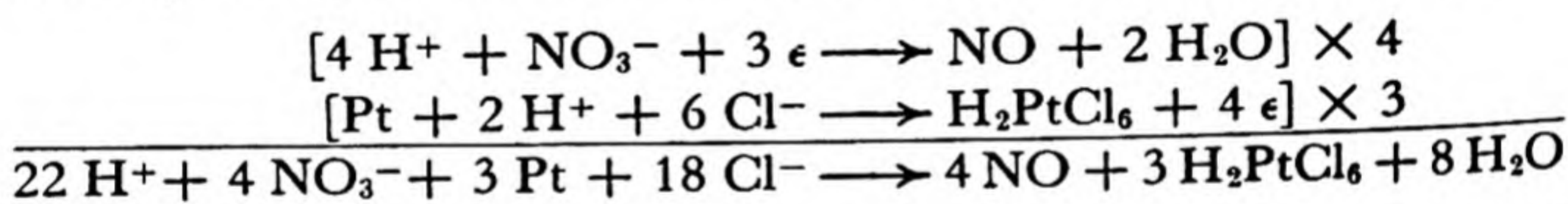
Nitrous Acid. This acid may be prepared by the addition of dilute sulfuric acid to a cold dilute solution of a nitrite.

$$NO_2^- + H^+ \rightleftharpoons HNO_2$$
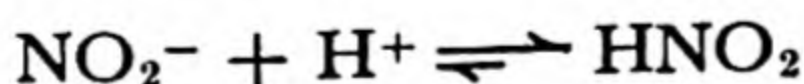
Solutions of the acid are blue. Nitrous acid is a weak acid which is unstable toward heat, decomposing at room temperature into a mixture of nitric oxide, nitrogen dioxide, and water.

$$2\,HNO_2 \rightleftharpoons H_2O + NO + NO_2$$
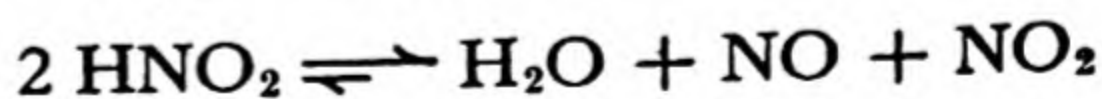
The anhydride of nitrous acid, *nitrogen trioxide*, N_2O_3, may be condensed from an equimolal mixture of these two oxides of nitrogen.

$$NO + NO_2 \rightleftharpoons N_2O_3$$
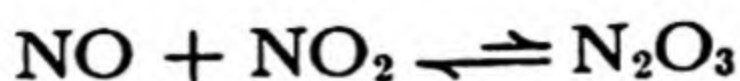
This oxide is a blue liquid which boils at $3.5°$. Nitrous acid also decomposes to form nitric acid and nitric oxide, showing that these

products of an auto-oxidation-reduction are more stable than nitrous acid.

$$3 \, HNO_2 \longrightarrow H^+ + NO_3^- + 2 \, NO + H_2O$$

Nitrous acid is an active oxidizing agent, the standard oxidation-reduction potential being $+ \, 0.99$ volt at $25°$. It causes the oxidation of iodides to iodine.

$$
\begin{array}{c}
[HNO_2 + H^+ + 1\,\epsilon \longrightarrow H_2O + NO] \times 2 \\
2 \, I^- \longrightarrow I_2 + 2 \, \epsilon \\
\hline
2 \, HNO_2 + 2 \, H^+ + 2 \, I^- \longrightarrow 2 \, NO + I_2 + 2 \, H_2O
\end{array}
$$
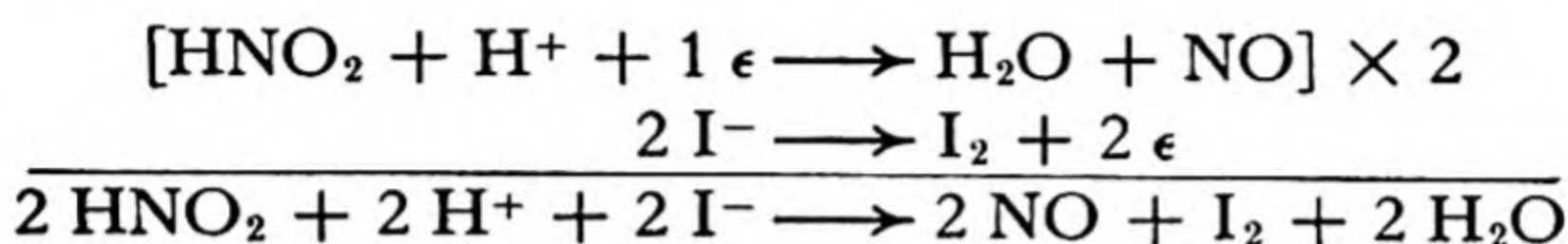
Test for Nitrates. A delicate test for the presence of nitrates is based on the oxidizing action of the nitrate ion in acidic solution. Nitric oxide, the reduction product, reacts with ferrous ions to form a dark brown addition product, $Fe(NO)^{++}$. The substance to be tested is dissolved in concentrated sulfuric acid in a test tube or cylinder, and a solution of ferrous sulfate is added slowly so as to form a separate layer above the more dense acid. In the presence of nitrates, a brown ring is formed at the juncture of the two liquids.

$$
\begin{array}{c}
4 \, H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2 \, H_2O \\
Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon \times 3 \\
\hline
4 \, H^+ + NO_3^- + 3 \, Fe^{++} \longrightarrow NO + 3 \, Fe^{+++} + 2 \, H_2O
\end{array}
$$
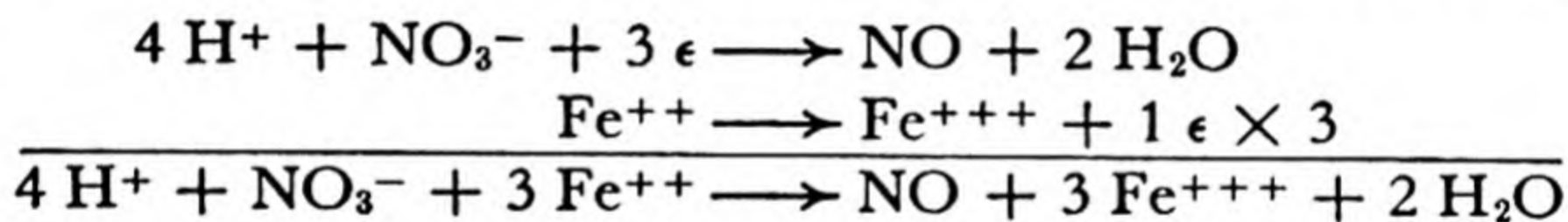
Nitrites also yield nitric oxide when they are reduced and, consequently, this test does not distinguish the two. Since nitrous acid is a weak and unstable acid, the nitrite ion may be removed before applying the nitrate test by adding dilute sulfuric acid and heating to drive out the oxides of nitrogen. However, a portion of the nitrous acid decomposes to form nitric acid during the heating. Consequently, the brown ring test is not fully satisfactory to distinguish the presence of nitrates in a solution containing nitrites.

The Oxides of Nitrogen. Nitrogen yields a series of oxides in which it exhibits oxidation numbers from $1 +$ to $5 +$. The anhydrides of nitrous acid and nitric acid may be prepared by the dehydration of the acids. These oxides decompose rapidly with the formation of other oxides and therefore they are not important. The other three oxides, nitrous oxide, nitric oxide, and nitrogen dioxide, are important.

Nitrous Oxide. **N₂O.** This oxide was first prepared by Priestley in 1772 by the reduction of nitric oxide with moist iron filings. Nitrous oxide is now prepared by gentle heating of ammonium nitrate. (Fig. 98.)

$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O \uparrow + 9{,}000 \text{ cal.}$$
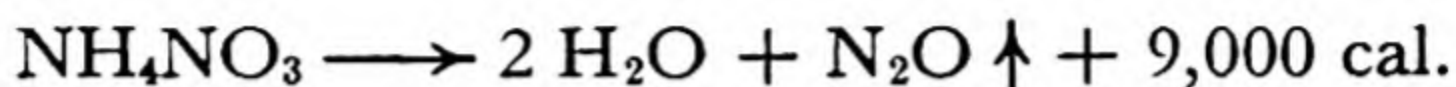
The decomposition of nitrous oxide into elements is also exothermic, and nitrous oxide is unstable toward heat. However, the rate of decomposition at ordinary temperatures is low.

$$2\,N_2O \longrightarrow 2\,N_2 + O_2 + 38{,}000 \text{ cal.}$$

If it is heated too strongly or is detonated, ammonium nitrate decomposes as a high explosive into nitrogen, oxygen, and water.
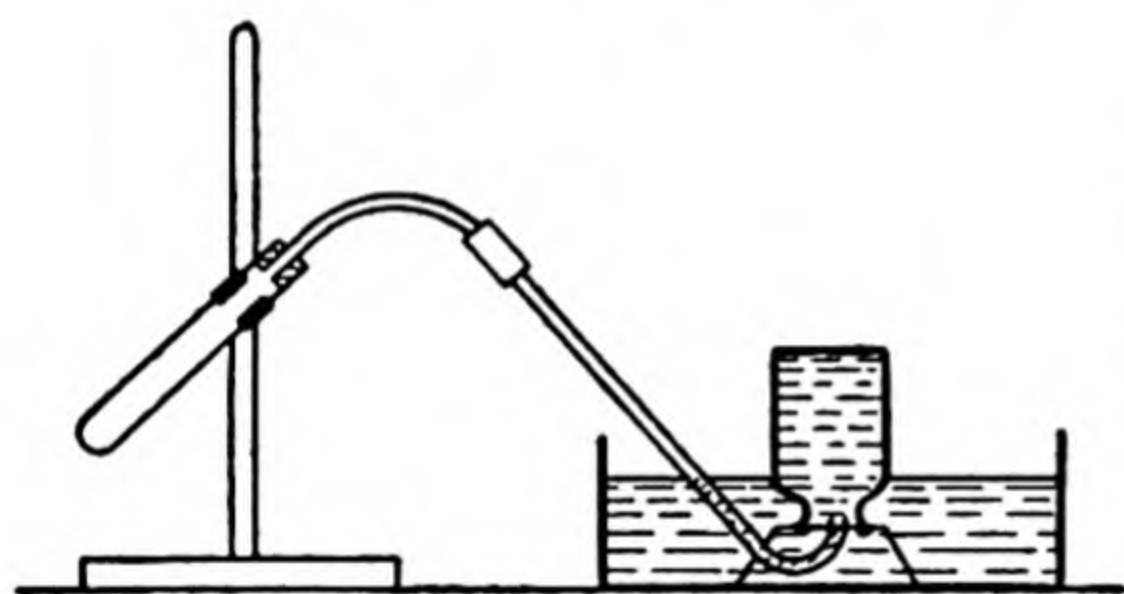
Fig. 98. *Laboratory Preparation of Nitrous Oxide*

Nitrous oxide is a colorless gas with a critical temperature of 35°. It may be liquefied by a pressure of 50 atmospheres at 20°. Its solubility in water is 130 volumes in 100 of water at 20° and at a gas pressure of 760 mm. Nitrous oxide readily supports combustion, yielding free nitrogen and the oxides of the elements in the substance burned. It does not cause the rusting of metals and does not support respiration. A small quantity of the nitrous oxide in a sample of this gas is decomposed when a burning splinter is introduced, and the reaction at the surface of the burning material continues because the decomposition reaction is itself exothermic. This gas is extensively used as an anaesthetic in dentistry and in some other surgical operations. The name "laughing gas" originated from the fact that the inhalation of small quantities of the gas produces a mild form of hysteria.

Nitric Oxide. **NO.** This oxide of nitrogen is usually prepared in the laboratory by the reaction of nitric acid with metals, such as copper. (Fig. 99.) Usually, the gas produced in this manner contains small proportions of other reduction products of the acid. Nitric oxide is the most stable nitrogen oxide toward heat and

toward the action of reducing agents. It does not readily support combustion, although active substances such as phosphorus may be burned in an atmosphere of the gas. The formation of nitric oxide is important as an intermediate step in the conversion of ammonia into nitric acid. The most important reaction of nitric oxide is with oxygen to produce nitrogen dioxide.

Fig. 99. *Laboratory Preparation of Nitric Oxide*

Nitrogen Dioxide. **NO₂.** This brown gas is produced by the combination of nitric oxide with oxygen. Hence, brown fumes are usually observed in the air above the liquid during the reaction of nitric acid with metals, even though nitric oxide may be the direct product. Nitrogen dioxide may be formed as the direct product of the reduction of concentrated nitric acid. Nitrogen dioxide may also be formed by the decomposition of the nitrates of the common metals, with the exception of sodium and potassium.

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

At temperatures between 150° and 620°, nitrogen dioxide partially decomposes to form an equilibrium mixture with nitric oxide and oxygen. The decomposition is complete at 620°.

$$2\,NO_2 \rightleftharpoons 2\,NO + O_2$$
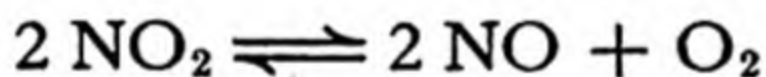
At 22°, about 75 per cent of the substance exists in the form of the tetroxide, N₂O₄, a polymer of nitrogen dioxide.

$$2\,NO_2 \rightleftharpoons N_2O_4$$

The most important reaction of nitrogen dioxide is with water.

EXERCISES

1. Discuss the relative importance of elementary nitrogen and of its compounds.
2. List important chemical reactions of nitrogen. Which of these reactions are employed for the industrial production of nitrogen compounds?
3. What conditions are employed in the synthetic processes for the production of ammonia? Explain in terms of the principles applying to chemical equilibrium why these conditions are selected.

4. Describe the cyanamide process for the fixation of atmospheric nitrogen. Mention important compounds produced by the use of this process as the first step.
5. How is ammonia produced from coal?
6. Write equations to represent important reactions of ammonia.
7. Discuss the equilibria in a solution of ammonia and account for the effect of adding to such a solution (*a*) an acid, (*b*) a strong base, (*c*) an ammonium salt, (*d*) a cupric salt.
8. How is nitric acid produced from ammonia? Give reasons for the conditions.
9. In the production of nitric acid from sodium nitrate, what is the advantage of using an excess of sulfuric acid? a reduced pressure?
10. What is meant by esterification? nitration? Represent each of these types of reactions by equations. Discuss the importance of these products of the reaction of nitric acid.
11. Write ionic equations to represent the general acidic reactions of nitric acid. Why is hydrogen not the usual product of the reaction of nitric acid with a metal?
12. Using the ion-electron method, derive the equations for the reactions of nitric acid with each of the following substances: (*a*) iodine; (*b*) copper; (*c*) sodium bromide; (*d*) sodium sulfite; (*e*) lead sulfide; (*f*) bismuth; (*g*) sodium chloride; (*h*) phosphorus; (*i*) arsenic trioxide; (*j*) ammonium chloride.
13. What is aqua regia? Write the equation to represent its reaction with gold to form chlorauric acid, $HAuCl_4$.
14. List the oxides of nitrogen and show how they illustrate the law of multiple proportions.
15. What is the source of nitrous oxide? nitric oxide? nitrogen dioxide?
16. What is the most important reaction of each of these oxides?

SUPPLEMENTARY READINGS

Curtis, H. A., *Fixed Nitrogen*, Reinhold Publishing Corporation, New York, 1932.

Furnas, C. C., *Rogers Manual of Industrial Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, chap. 8.

Badger, W. L., and E. M. Baker, *Inorganic Chemical Technology*, McGraw-Hill Book Company, Inc., New York, 1941, chap. IV.

Mellor, J. W., *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Company, New York, 1922, Vol. VIII.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 2, 6.

Curtis, H. A., "Nitrogen Fixation," *J. Chem. Education* **19**, 161 (1942).

Miller, A. M., and J. N. Judkins, "Nitrogen Fixation at the TVA Ammonia Plant," *Chem. Met. Eng.* **50**, 11, 119 (1943).

Smith, A. M., "New Horizons in Nitrogen," *Chem. Eng. News* **21**, 215 (1943).

"Ammonia Synthesis at TVA," Pictured Flow Sheet, *Chem. Met. Eng.* **50**, 11, 152 (1943).

"Production of Cyanamide," Pictured Flow Sheet, *Chem. Met. Eng.* **47**, 4, 253 (1940).

Chapter 22

THE PHOSPHORUS FAMILY OF ELEMENTS

The four elements, *phosphorus, arsenic, antimony,* and *bismuth* are in Group V of the periodic system along with nitrogen, the element of lowest atomic weight in this group. These elements make up a natural family that exhibits a transition from the nonmetallic properties of the elements of lower atomic numbers to the metallic properties of those of higher atomic numbers. The atoms of these elements contain five valence electrons, and the elements exhibit a maximum positive oxidation number of 5 and a negative number of 3 in various compounds. They also form compounds in intermediate stages of oxidation.

PHOSPHORUS

The natural source of phosphorus and its compounds is calcium phosphate in the mineral *phosphorite.* Large deposits of this mineral are found in the United States in Florida, Tennessee, Montana, and other states, in northern Africa, and in many other parts of the world. Calcium phosphate is the principal mineral constituent of bones, and complex organic compounds containing this element are present in muscles, nerves, and brain tissue. Compounds of phosphorus are contained in many foods such as eggs, beans, peas, and wheat.

Preparation of Phosphorus. The element is prepared by heating a mixture of calcium phosphate, sand, and coke in an electric furnace.

$$Ca_3(PO_4)_2 + 5\,C + 3\,SiO_2 \longrightarrow 3\,CaSiO_3 + 2\,P + 5\,CO$$
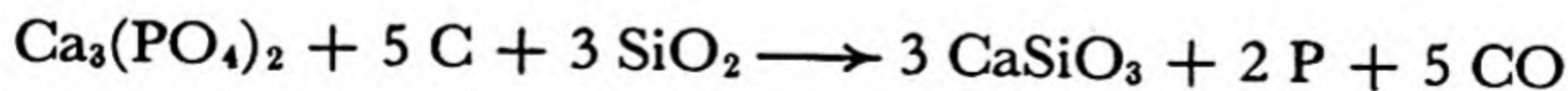
The charge is fed continuously into the furnace (Fig. 100) from the hopper at the top. Melted calcium silicate is drawn off as slag from time to time through the outlet S. Gaseous phosphorus and

357

carbon monoxide emerge from the furnace at *G*, and phosphorus is condensed.

Properties of Phosphorus. There are two familiar forms of phosphorus. *White phosphorus*, the more active variety, is a soft, wax-like solid having a specific gravity of 1.82 at 20° and a melting point of 44.1°. It is obtained by condensing phosphorus vapor. This form of phosphorus is soluble in carbon disulfide but is practically insoluble in water. White phosphorus vaporizes rapidly at ordinary temperatures. It is very poisonous and the effects are cumulative, resulting in chronic poisoning if one remains long in an atmosphere containing the vapor. One of its harmful effects is necrosis or decay of

Fig. 100. Production of Phosphorus

bones, particularly the jaw bone. If left exposed to air, white phosphorus ignites spontaneously. Hence, it must be stored and worked out of contact with air, frequently beneath the surface of water.

Red phosphorus has no definite melting point or density. It sublimes when heated at atmospheric pressure. It is insoluble in both water and carbon disulfide and is not poisonous. Red phosphorus is not a single variety but appears to be a mixture of the white and a more stable variety known as *violet phosphorus*. There is no specific transition temperature between these modifications. White phosphorus slowly changes into the red variety. The rate of change is increased in light and at higher temperatures.

Reactions of Phosphorus. Phosphorus unites directly with oxygen, with sulfur, with the halogens, and with many metals. In all these reactions, the less stable white variety reacts more vigorously than the more stable red modification. White phosphorus oxidizes slowly at room temperatures and becomes ignited at about 45°, while the red modification must be heated to 240° to burn in air. The slow oxidation of phosphorus to the trioxide is accompanied by the emission of a greenish yellow light, a phe-

nomenon known as *phosphorescence*. When phosphorus burns in an excess of air, the pentoxide is produced:

$$4 P + 5 O_2 \longrightarrow 2 P_2O_5$$
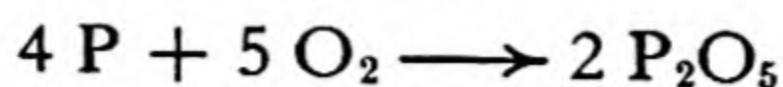
The trihalide is first formed by the direct union of the element with the halogens. It combines with an excess of the halogen to form the pentahalide, except with iodine which does not yield a pentiodide

$$2 P + 3 Cl_2 \longrightarrow 2 PCl_3$$
$$PCl_3 + Cl_2 \longrightarrow PCl_5$$
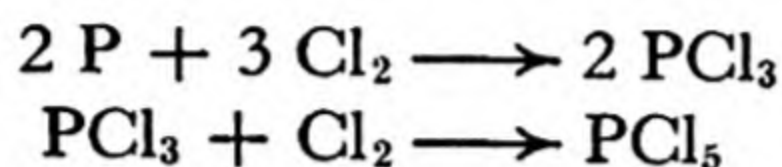
There are several sulfides of phosphorus that may be prepared by the direct union of the elements mixed in proper proportions. Among these, the sulfides of the composition P_4S_3 and P_2S_5 are the more important.

$$4 P + 3 S \longrightarrow P_4S_3$$
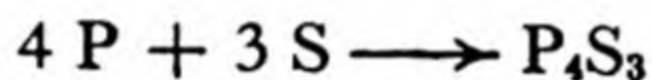
The direct union of phosphorus with the metals produces binary compounds known as phosphides.

$$3 Ca + 2 P \longrightarrow Ca_3P_2$$
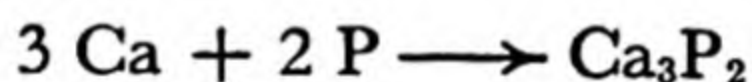
Phosphorus yields phosphoric acid when it reacts with solutions of the acidic oxidizing agents.

$$[4 H^+ + NO_3^- + 3 \epsilon \longrightarrow 2 H_2O + NO] \times 5$$
$$\underline{[P + 4 H_2O \longrightarrow H_3PO_4 + 5 H^+ + 5 \epsilon] \times 3}$$
$$5 H^+ + 5 NO_3^- + 3 P + 2 H_2O \longrightarrow 5 NO + 3 H_3PO_4$$
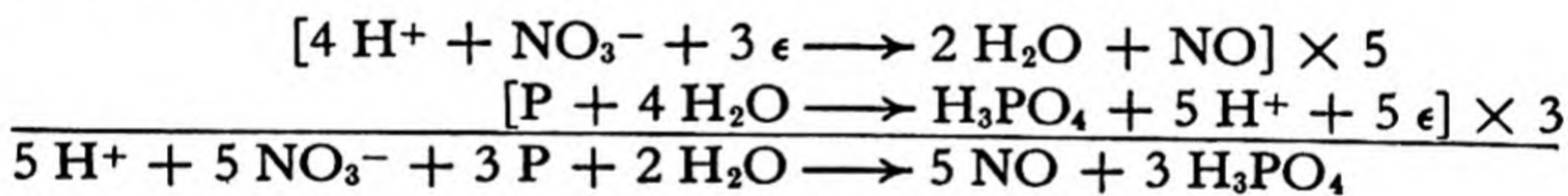
Uses of Elementary Phosphorus. The most extensive use of elementary *phosphorus* is in the manufacture of *matches*. The head of a match contains a mixture of an oxidizing agent and a substance of low kindling temperature. Formerly, white phosphorus was extensively used as the substance of low kindling temperature, but its use is now prohibited because of its poisonous nature, and the sulfide, P_4S_3, is used in the common match. The ends of match sticks are dipped into a paste containing an oxidizing agent, such as lead dioxide, potassium chlorate, or potassium nitrate, and the sulfide of phosphorus together with powdered glass, dextrin, and glue. When the match head is dry, it is coated with varnish to exclude moisture and air. The mixture is easily ignited by friction. The "double dip" matches contain the phosphorus compound

only in the tip, the larger portion of the match head being made up of a combustible substance, such as antimony sulfide, or organic material and an oxidizing agent. Safety matches contain none of the phosphorus compound, but the striking surface on the box contains red phosphorus, dextrin, and a filler such as powdered glass. The match head is composed of a good oxidizing agent and antimony trisulfide. This match head is brittle and cannot ordinarily be ignited by scratching it against a rough surface. When it is rubbed against the specially prepared striking surface, a trace of red phosphorus on this surface is ignited, and this starts the combustion of the substances in the match head.

Phosphorus was used during World War I in tracer bullets and for the production of smoke screens. White phosphorus is used extensively in incendiary shells, bombs, and leaves. The element has important uses in the production of some of its compounds.
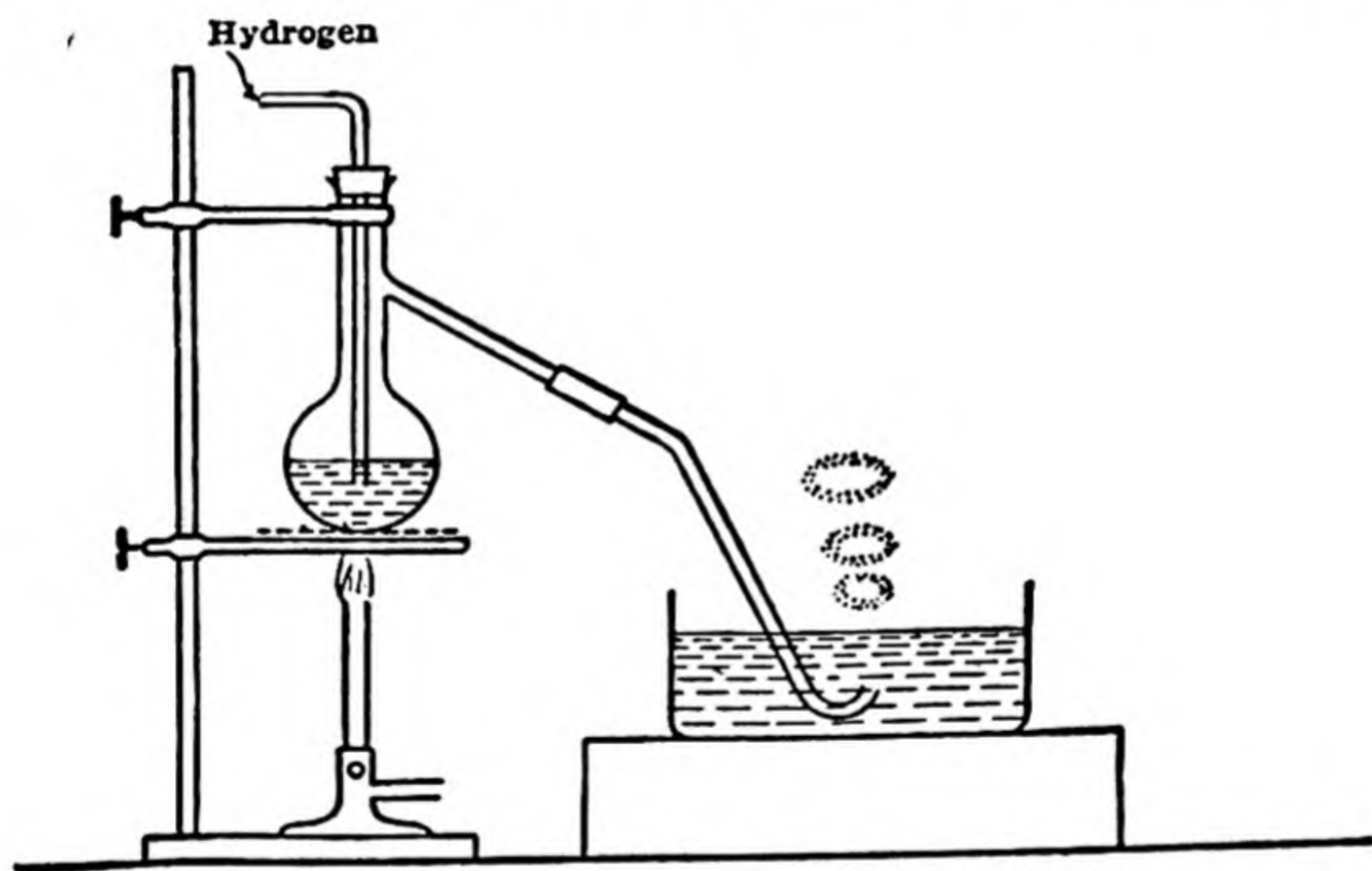
Fig. 101. Preparation of Phosphine

Hydrides of Phosphorus. Phosphorus does not unite directly with hydrogen, but *phosphine*, PH_3, may be prepared by the hydrolysis of calcium phosphide.

$$Ca_3P_2 + 6 H_2O \longrightarrow 3 Ca(OH)_2 + 2 PH_3$$
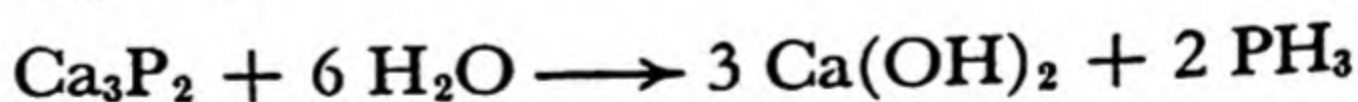
Phosphine may be prepared also by the reaction of white phosphorus with a hot solution of a strong base.

$$4 P + 3 OH^- + 3 H_2O \longrightarrow PH_3 + 3 H_2PO_2^-$$

Phosphine prepared in this manner contains a small proportion of the hydride P_2H_4, which is spontaneously combustible in air. In order to prevent an explosion during the laboratory preparation of phosphine, the air in the reaction flask is displaced by a current of hydrogen. (Fig. 101.) The gas then burns spontaneously as it is delivered into air, with the formation of a white smoke consisting of small solid particles of phosphorus pentoxide.

$$2 PH_3 + 4 O_2 \longrightarrow P_2O_5 + 3 H_2O$$

Phosphine is a colorless gas, insoluble in water. It is highly poisonous.

Halides of Phosphorus. Phosphorus combines with the halogens, producing trihalides and pentahalides. The pentiodide is not produced, but an iodide with the composition P_2I_4 may be prepared in addition to the triiodide. These compounds react with water, forming the corresponding hydrohalic acid and the oxyacid of phosphorus. *Phosphorus trichloride*, the first product of the reaction of the element with chlorine, is a colorless liquid which boils at 75.5°. With an excess of chlorine, *phosphorus pentachloride*, a white solid, is produced. The solid sublimes when it is heated at atmospheric pressure. It is partially decomposed into the trichloride and chlorine, and the gaseous mixture at 250° contains only 20 per cent of the pentachloride.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The halides react vigorously with water and fume in moist air because of the formation of hydrogen chloride.

$$PCl_3 + 3 H_2O \longrightarrow 3 HCl + H_3PO_3$$
$$PCl_5 + 4 H_2O \longrightarrow 5 HCl + H_3PO_4$$
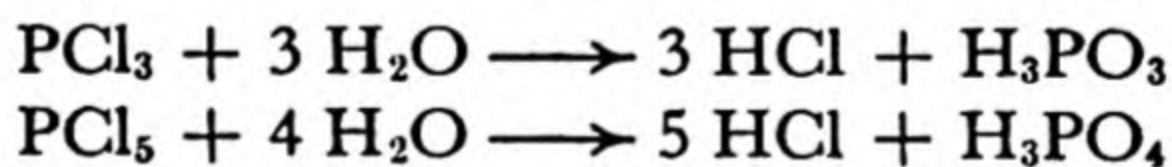
They also react with other substances containing the hydroxide radical, such as ethanol, C_2H_5OH.

$$PCl_3 + 3 C_2H_5OH \longrightarrow 3 C_2H_5Cl + H_3PO_3$$
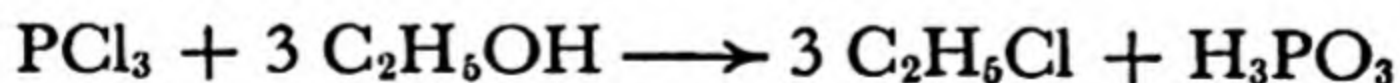
Oxides of Phosphorus. There are three oxides of phosphorus, the trioxide, the tetroxide, and the pentoxide. The tetroxide is not important. The oxides and acids of phosphorus are summarized in Table 30.

TABLE 30. OXIDES AND ACIDS OF PHOSPHORUS

Oxides	Formula	Acids	Formula
		Hypophosphorous	H_3PO_2
Trioxide	P_2O_3	Orthophosphorous	H_3PO_3
		Pyrophosphorous	$H_4P_2O_5$
		Hypophosphoric	$H_4P_2O_6$
		Orthophosphoric	H_3PO_4
Pentoxide	P_2O_5	Pyrophosphoric	$H_4P_2O_7$
		Metaphosphoric	HPO_3

Phosphorus trioxide, P_2O_3, is formed when phosphorus is burned in a limited supply of air. Some phosphorus pentoxide is formed at the same time, but the trioxide is more volatile than the pentoxide, and the two may be separated by passing the combustion products through a plug of glass wool, thus filtering out the solid phosphorus pentoxide. Phosphorus trioxide condenses to a white solid which melts at 23.8°. It reacts slowly with cold water to form phosphorous acid, and with strong bases to form phosphites.

$$P_2O_3 + 3\,H_2O \longrightarrow 2\,H_3PO_3$$
$$P_2O_3 + 4\,OH^- \longrightarrow 2\,HPO_3^{--} + H_2O$$
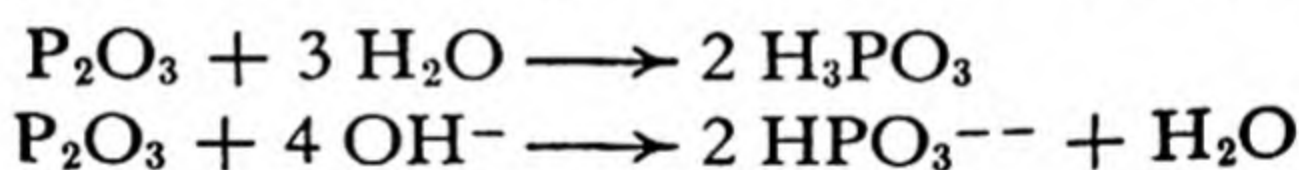
When heated in a sealed tube, phosphorus trioxide yields a mixture of the tetroxide and the elementary phosphorus.

$$4\,P_2O_3 \longrightarrow 3\,P_2O_4 + 2\,P$$
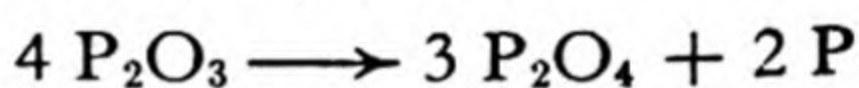
Phosphorus pentoxide, P_2O_5, is formed as a dense white smoke when phosphorus and its combustible compounds are burned in an excess of oxygen or air. The solid sublimes when heated. The oxide reacts vigorously with water to form metaphosphoric acid, HPO_3, as the principal product.

$$P_2O_5 + H_2O \longrightarrow 2\,HPO_3$$
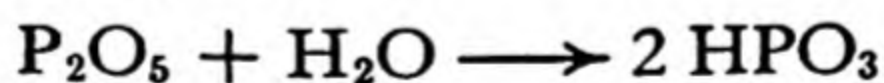
The pressure of water vapor in the air in contact with phosphorus pentoxide is so low that the substance is an excellent drying agent.

Hypophosphorous Acid. $H(H_2PO_2)$. Salts of hypophosphorous acid are produced by the reaction of elementary phosphorus with soluble metal hydroxides, with the evolution of gaseous phosphine. The acid is easily prepared by the reaction of sulfuric acid with barium hypophosphite.

$$Ba^{++} + 2H_2PO_2^- + 2H^+ + SO_4^{--} \longrightarrow BaSO_4 \downarrow + 2H_3PO_2 + 2H_2O$$
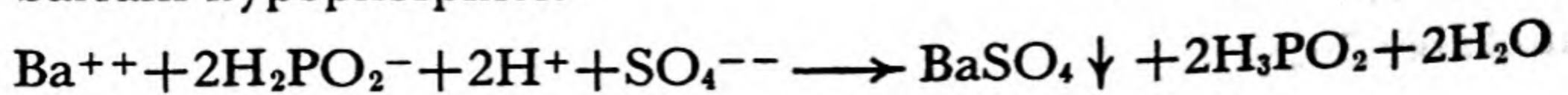
The acid contains only one replaceable hydrogen atom.

$$H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$$
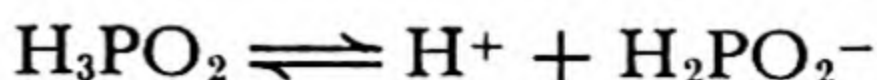
Phosphorous Acid. $H_2(HPO_3)$. Three acids contain phosphorus in the oxidation state of 3 +. Since only one of these is important, it is commonly called phosphorous acid without distinguishing it from the other two. This acid is formed by the reaction of phosphorus trioxide with cold water and by the hydrolysis of phosphorus trichloride. The phosphorous acid molecule contains two replaceable hydrogen atoms.

$$H_3PO_3 + 2\,OH^- \rightleftharpoons 2\,H_2O + HPO_3^{--}$$
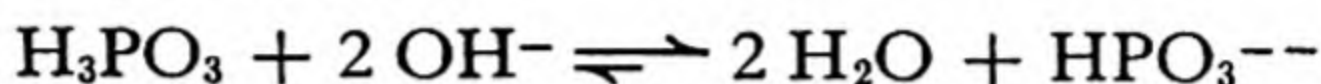
This reaction indicates that two of the hydrogen atoms are members of hydroxide groups with polar covalent bonds, while the third hydrogen atom is bound directly to the phosphorus atom in a non-
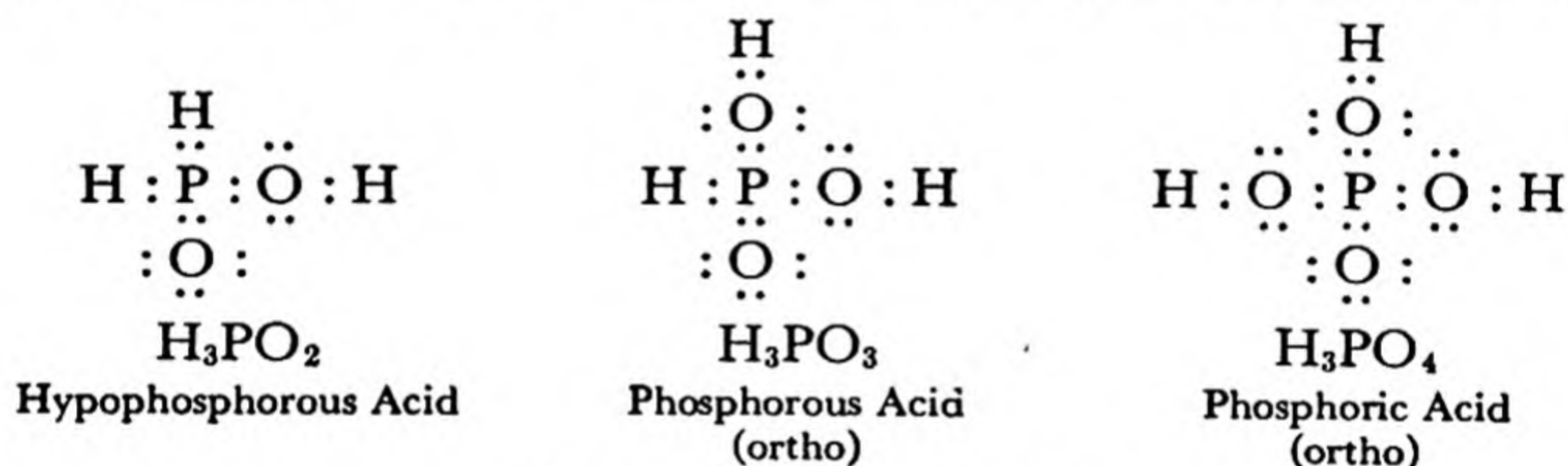
Fig. 102. Electronic Formulas

polar bond. The structural relationships of hypophosphorous acid, phosphorous acid, and phosphoric acid are shown by the electronic formulas in Fig. 102. Phosphorous acid is oxidized by nitric acid with the formation of phosphoric acid.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 2$$
$$\underline{[H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2\,H^+ + 2\,\epsilon] \times 3}$$
$$2\,H^+ + 2\,NO_3^- + 3\,H_3PO_3 \longrightarrow 2\,NO + 3\,H_3PO_4 + H_2O$$
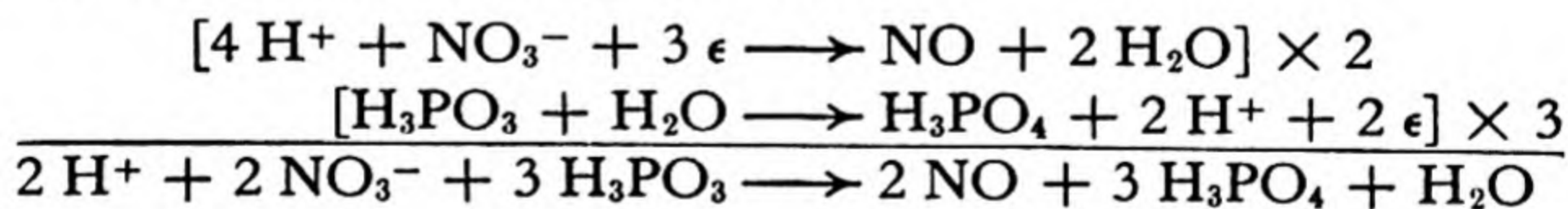
Phosphorous acid decomposes when heated to form phosphine and phosphoric acid, showing greater oxidation-reduction stability of the element in the high and low states of oxidation than in an intermediate state.

$$4\,H_3PO_3 \longrightarrow PH_3 + 3\,H_3PO_4$$
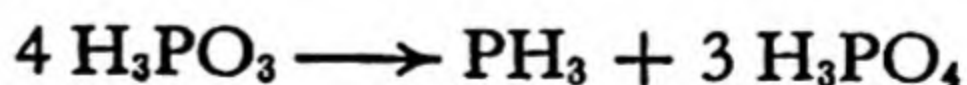
The Phosphoric Acids. Three acids contain phosphorus in the high oxidation state, 5 +, and all three are phosphoric acids.

Phosphorus pentoxide is the anhydride of the three acids, but the acids differ in the degree of hydration. The prefix *ortho-* is used to designate the common acid in the highest degree of hydration. The *meta-* acid commonly differs from the *ortho-* acid by one mole of water per mole of the acid, and the *pyro-* acid is intermediate. Orthophosphoric acid has the composition, H_3PO_4; pyrophosphoric acid, $H_4P_2O_7$; and metaphosphoric acid, HPO_3. When orthophosphoric acid is heated at 215°, it decomposes slowly, forming pyrophosphoric acid, and the dehydration proceeds further at 400°, with the formation of metaphosphoric acid.

$$2\ H_3PO_4 \longrightarrow H_2O + H_4P_2O_7$$
$$H_4P_2O_7 \longrightarrow H_2O + 2\ HPO_3$$
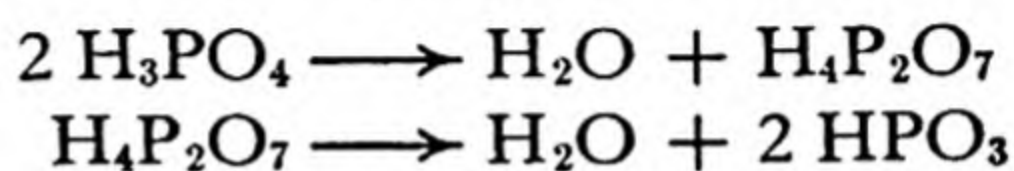
Orthophosphoric acid is the only one of these compounds having extensive uses.

Orthophosphoric acid, $\mathbf{H_3PO_4}$, is commonly called phosphoric acid. It may be prepared by the reaction of nitric acid with phosphorus and by the reaction of phosphorus pentoxide with an excess of water. Metaphosphoric acid, the direct product of the reaction of the oxide with water, is hydrated to produce phosphoric acid by heating the solution with nitric acid which serves as a catalyst. The product is concentrated by evaporation.

$$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4$$

Impure phosphoric acid, suitable for many industrial uses, may be prepared by mixing pulverized phosphate rock with sulfuric acid of specific gravity of 1.5, and heating the mixture with steam.

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 3\ CaSO_4 + 2\ H_3PO_4$$
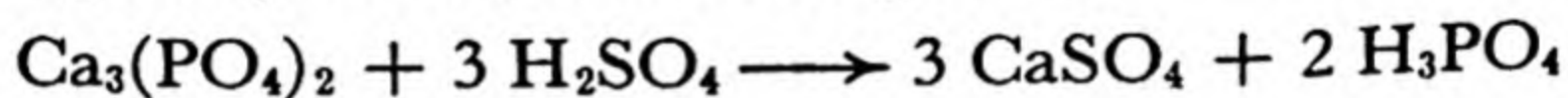
The precipitated calcium sulfate is removed by filtration, and the solution is concentrated by evaporation. Phosphoric acid is now produced by an electric furnace process. Phosphorus vapor, produced as described previously, is burned to form the pentoxide. The pentoxide is then absorbed in water.

The pure acid is a solid which melts at 42.3°. There is also a crystalline hydrate, $(H_3PO_4)_2H_2O$, which melts at 29.4°. Commercial grades of the acid contain varying proportions of water. The solution containing 85–88 per cent of the acid is a syrupy liquid having a specific gravity of about 1.7.

Phosphoric acid is a moderately weak acid that ionizes in three stages. The primary ionization is the principal stage in 0.1 N. solution.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$
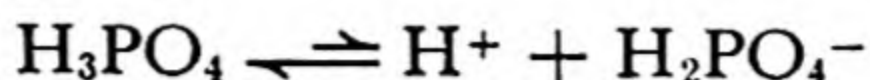
The dihydrogen phosphate ion is only weakly ionized, and the monohydrogen phosphate ion is ionized but slightly.

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$$
$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$$
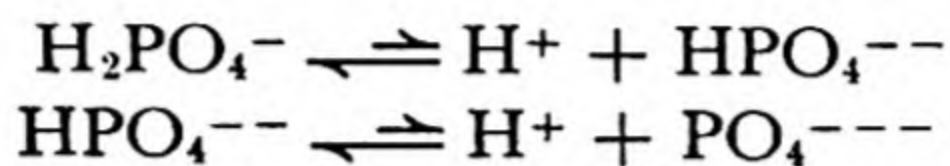
The concentration of the phosphate ion in acidic solutions is slight.

Phosphates. The normal salts of phosphoric acid are only slightly soluble, with the exception of the phosphates of sodium, potassium, and ammonium. The hydrophosphate salts are, in general, more soluble than normal salts. The soluble phosphates are commonly prepared by the reaction of phosphoric acid with the appropriate metal hydroxide or carbonate. The hydrophosphates are produced by the reaction of the acid with calculated proportions of the basic substance, and by the reaction of a stronger acid with the normal phosphate. Mixed salts may be obtained by the reaction of the acid with different basic substances in the right proportions. The insoluble phosphates are commonly prepared by precipitation.

Phosphates of Sodium. The reaction of sodium hydroxide with phosphoric acid may produce the dihydrogen phosphate, the monohydrogen phosphate, or the normal phosphate, depending on the proportions of the acid and base.

$$H_3PO_4 + OH^- \rightleftharpoons H_2O + H_2PO_4^-$$
$$H_2PO_4^- + OH^- \rightleftharpoons H_2O + HPO_4^{--}$$
$$HPO_4^{--} + OH^- \rightleftharpoons H_2O + PO_4^{---}$$
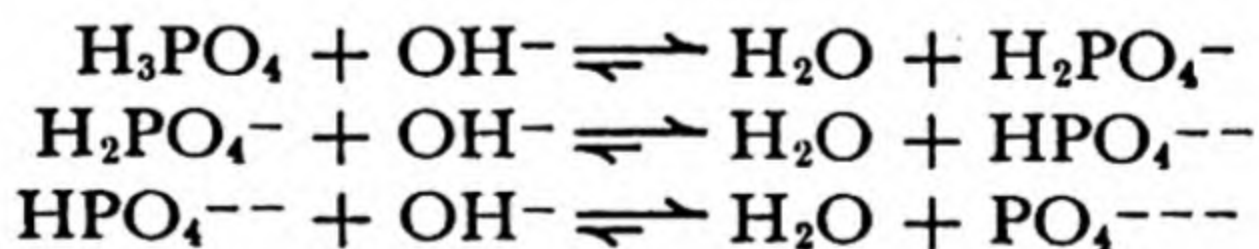
Sodium dihydrogen phosphate is weakly acidic in solution, but the monohydrogen phosphate and the normal phosphate are basic because of the hydrolysis of these anions.

Sodium dihydrogen phosphate is used as the acidic substance in some baking powders, and some of the phosphates are used medicinally. Trisodium phosphate is used in water treatment for the removal of acidic substances and in some soap powders. Sodium ammonium hydrogen phosphate, $NaNH_4HPO_4$, known as

microcosmic salt, and sodium dihydrogen phosphate are the common laboratory reagents used to supply phosphate ions.

Effect of Heating Phosphates. The normal phosphates are not easily decomposed by heat, but the hydrophosphates and the salts containing ammonium ions decompose when they are heated. Dihydrogen phosphates are decomposed to form metaphosphates. Microcosmic salt also yields the metaphosphate.

$$NaH_2PO_4 \longrightarrow H_2O + NaPO_3$$
$$NaNH_4HPO_4 \longrightarrow H_2O + NH_3 + NaPO_3$$
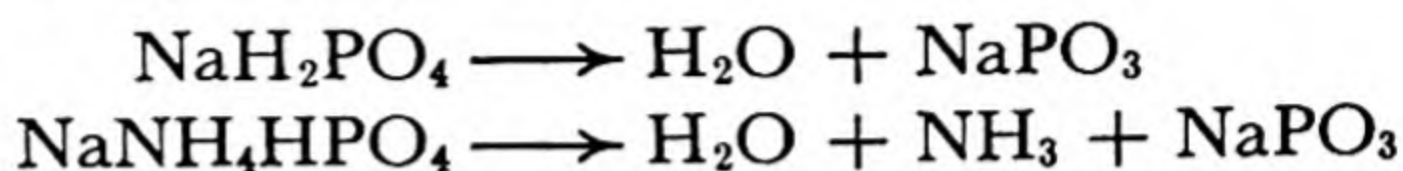
Monohydrogen phosphates decompose when heated to form pyrophosphates.

$$2\,Na_2HPO_4 \longrightarrow H_2O + Na_4P_2O_7$$

Both metaphosphates and pyrophosphates in the melted state react with basic substances in the same manner as acidic oxides. Some of the mixed salts produced in this reaction have distinctive colors, *e.g.*, the blue cobalt salt.

$$NaPO_3 + CoO \longrightarrow NaCoPO_4$$
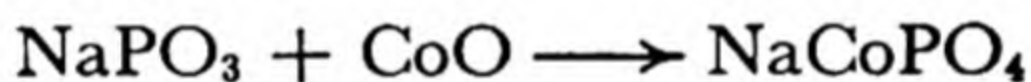
This reaction is sometimes employed as a test for certain metal ions.

Phosphates of Calcium. Phosphate Fertilizers. Calcium phosphate is the most important of the phosphates. Approximately 5 million tons of phosphate rock were mined in the United States in 1942 for the production of phosphate fertilizers, phosphoric acid, and elementary phosphorus. The naturally occurring normal calcium phosphate is not soluble and, consequently, is not suitable for direct use as a fertilizer. Calcium dihydrogen phosphate, however, is soluble and can furnish the phosphorus required by growing plants. This substance is prepared from the normal phosphate by the action of sulfuric acid. For this purpose, the chamber acid is suitable, since it is desirable to have enough water in the reacting mixture to hydrate the calcium sulfate and prevent the subsequent caking of the product.

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\,CaSO_4$$
$$2\,CaSO_4 + 4\,H_2O \longrightarrow 2\,CaSO_4(H_2O)_2$$
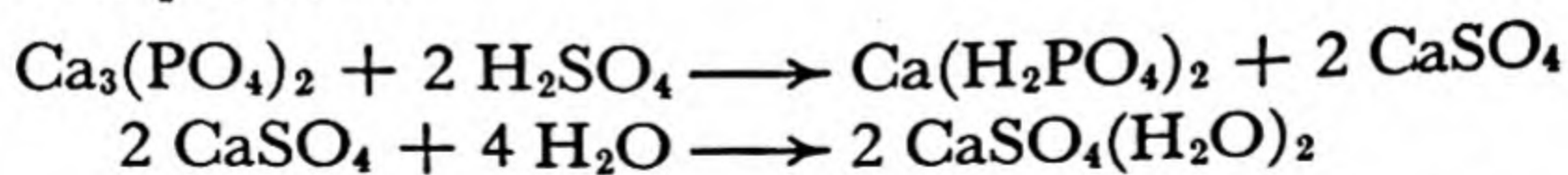
This mixture, known as *superphosphate of lime*, is extensively used as a fertilizer. The production of superphosphate in the United States in 1943 amounted to 6.5 million tons calculated on a basis

ᴏf a phosphate content equivalent to 18 per cent of phosphorus pentoxide. A more concentrated phosphate fertilizer is produced by the reaction of phosphoric acid with phosphate rock.

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \longrightarrow 3\ Ca(H_2PO_4)_2$$
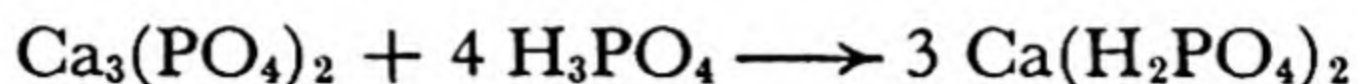
Ammonium phosphate is produced by the absorption of ammonia in phosphoric acid. This salt is especially valuable as a fertilizer, because it supplies both nitrogen and phosphorus in a form available for plants.

ARSENIC. ANTIMONY. BISMUTH

These three elements resemble each other more closely than phosphorus. In each series of similar compounds, a transition from the nonmetallic character of phosphorus to the metallic character of bismuth may be traced. Nonmetallic elements may yield simple electrovalent negative ions and complex negative ions, such as the oxyanions in which nonmetals have positive oxidation numbers, while metals yield electrovalent positive ions. The hydrolysis of the nonmetal halides is an irreversible process, but the hydrolysis of metal halides is characteristically reversible. The acid-base nature of the hydroxide likewise distinguishes nonmetallic and metallic elements. In the consideration of the transitions in this group of elements, the nature of the ions they yield, the properties of the products formed by hydrolysis of the halides, and the acidic, the amphoteric, or the basic nature of the hydroxides are especially significant.

Occurrence of Arsenic, Antimony, and Bismuth. Unlike phosphorus, these elements occur in the uncombined state and do not occur as salts of the oxyacids. The elementary occurrence of bismuth is the most important source of this metal. All of these metals occur to a limited extent in trioxides. Arsenic is found in arsenides of iron, cobalt, and nickel. However, the most extensive occurrence of these elements is in their sulfides: *arsenical pyrites,* FeAsS, *orpiment,* As_2S_3, *realgar,* AsS, *stibnite,* Sb_2S_3, and *bismuthinite,* Bi_2S_3. Naturally occurring materials used as sources of metals are called *ores.* Large quantities of arsenic are produced from the nickel and cobalt ores in Canada, and as a by-product in the

smelting of copper ores. Most of the supply of antimony has come from China in the past. Bismuth is obtained from Bolivia and from Canada, and it is also a by-product of the production of lead and copper from certain ores.

Preparation of Arsenic, Antimony, and Bismuth. Usually, the first step in the production of elements from their sulfides is the burning of the sulfide, a procedure known as *roasting* the ore. In specific instances other procedures may be employed. The roasting of sulfides of arsenic, antimony, and bismuth produces oxides.

$$2 As_2S_3 + 9 O_2 \longrightarrow 2 As_2O_3 + 6 SO_2$$
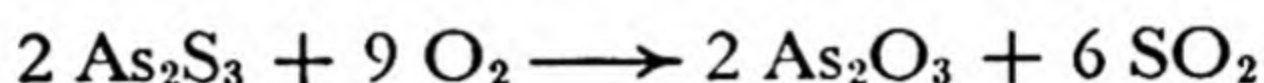
The oxides are then reduced by heating with carbon usually in the form of coke.

$$As_2O_3 + 3 C \longrightarrow 2 As + 3 CO$$
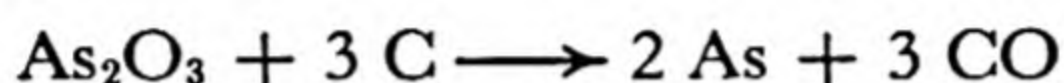
Bismuth may be separated from the ores, in which it occurs in uncombined state, by melting the metal and allowing the liquid to flow away from the rock.

Properties of Arsenic, Antimony, and Bismuth. Arsenic and antimony exist in more than one form. The active modification of *arsenic* is an unstable crystalline variety known as *yellow arsenic*, which is formed by the condensation of the vapor in cold carbon disulfide. This form of the element rapidly changes into the stable modification, *metallic arsenic*, which is gray in color and has a high luster. It is very brittle and may be easily powdered. It sublimes when heated under a pressure of one atmosphere.

Antimony exists in modifications similar to those of arsenic. The yellow variety is unstable except at low temperatures. The stable form of antimony at ordinary temperatures is a silvery white metal.

TABLE 31. PROPERTIES OF THE ELEMENTS OF THE PHOSPHORUS FAMILY

Property	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weight	31.02	74.91	121.76	209.00
Atomic number	15	33	51	83
Electron structure	2, 8, 5	2, 8, 18, 5	2, 8, 18, 18, 5	2, 8, 18, 32, 18, 5
Melting point (° C.)	44.1	814.0 [a]	630.5	271.0
Boiling point (° C.)	280	615 [b]	1380	1470
Specific gravity	1.82	5.7	6.68	9.8

[a] 36 atm.   [b] Sublimes.

Bismuth is known in only one solid form. It is a lustrous crystalline metal, grayish-white in color. The metal is hard and brittle.

Some of the specific properties of these elements, together with corresponding properties of phosphorus for comparison, are shown in Table 31.

Uses of Arsenic, Antimony, and Bismuth. *Elementary arsenic* has no extensive commercial uses. A small quantity of the element is used in the manufacture of lead shot. The presence of about 0.5 per cent of arsenic increases the surface tension of lead, and causes it to assume the spherical form when poured in molten state from a height in a shot tower. The use of arsenic also increases the hardness of the shot. Arsenic is added to some alloys to raise the annealing temperature, so that the product will not lose strength when heated as in welding.

The principal use of *antimony* is in the manufacture of its alloys. These alloys are hard and expand on solidification, so that they completely fill the mold and produce sharp castings. Type metal contains 82 per cent of lead, 15 per cent of antimony, and 3 per cent of tin; britannia metal, 90 per cent of tin and 10 per cent of antimony; babbitt metal, 90 per cent of tin, 7 per cent of antimony, and 3 per cent of copper; and antifriction metal, 75 per cent of tin, 12.5 per cent of antimony, and 12.5 per cent of copper. These compositions are typical of the alloys, but they may be varied considerably in making alloys for specific purposes. Approximately one half of the antimony used in the United States goes into the production of a lead alloy, containing about 6 per cent of antimony, for the manufacture of plates for storage batteries. It is also used as a hardening agent in lead sheaths for telephone cables, thus greatly decreasing maintenance costs.

Bismuth is employed in making alloys of low melting point, *e.g.*, Wood's metal, 50 per cent bismuth, 25 per cent lead, and 12.5 per cent each tin and cadmium. This alloy melts at about 71°. Alloys of different melting points may be prepared by varying the proportions of the components. Such alloys are useful as plugs in automatic fire extinguisher systems, and as safety plugs in steam boilers.

Reactions of the Elements. The elements burn in oxygen and in air with the formation of the trioxide.

$$4\,As + 3\,O_2 \longrightarrow 2\,As_2O_3$$
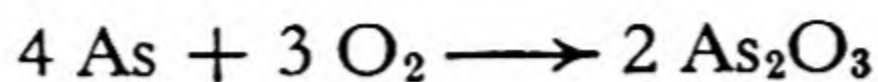
They also unite directly with the halogens and with sulfur, and the trivalent compound is the usual product of the reaction, but the pentavalent arsenic and antimony compounds may be formed with an excess of the halogen or sulfur.

$$2\,Sb + 3\,Cl_2 \longrightarrow 2\,SbCl_3$$
$$2\,Bi + 3\,S \longrightarrow Bi_2S_3$$
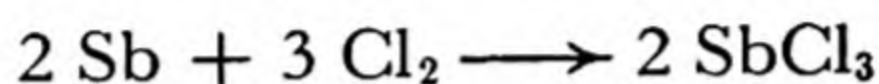
The elements unite directly with many of the metals at red heat to form binary compounds, known as arsenides, antimonides, and bismuthides, respectively.

$$3\,Zn + 2\,As \longrightarrow Zn_3As_2$$
$$3\,Mg + 2\,Sb \longrightarrow Mg_3Sb_2$$
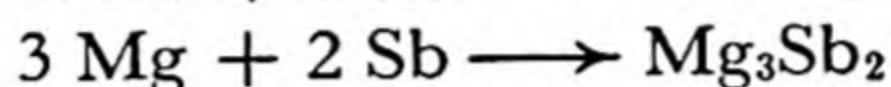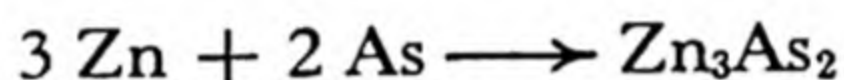
Bismuth does not form such compounds with other metals as readily as arsenic and antimony.

The elements react with nitric acid. Arsenic and antimony are oxidized to the 5 + state, producing weak acids. *Arsenic acid* is represented by the formula, H_3AsO_4, and the equation for the reaction is similar to that for the reaction of phosphorus with nitric acid. Antimony yields the compound known as *pyroantimonic acid*, $HSb(OH)_6$.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 5$$
$$[Sb + 6\,H_2O \longrightarrow HSb(OH)_6 + 5\,H^+ + 5\,\epsilon] \times 3$$
$$\overline{5\,H^+ + 5\,NO_3^- + 3\,Sb + 8\,H_2O \longrightarrow 5\,NO + 3\,HSb(OH)_6}$$
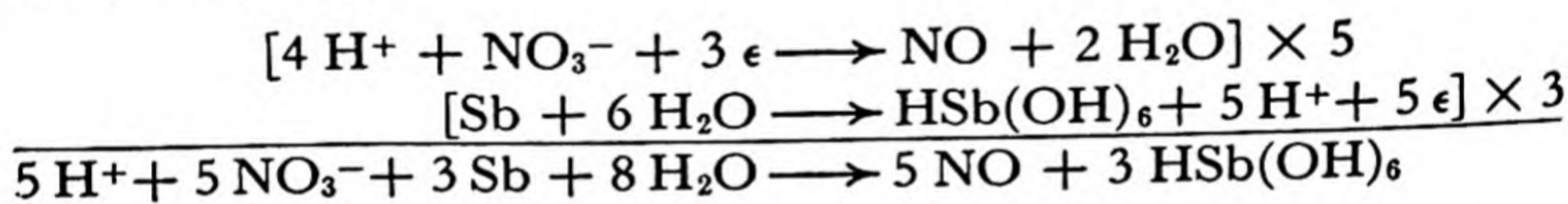
The reaction of bismuth with nitric acid yields the electrovalent bismuth ions having an oxidation number of 3 +.

$$4\,H^+ + NO_3^- + Bi \longrightarrow NO + Bi^{+++} + 2\,H_2O$$
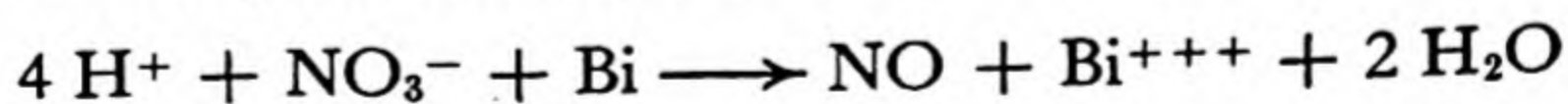
The nonmetallic nature of arsenic and antimony is shown by the formation of complex anions during the reaction of the elements with nitric acid. Similarly, the metallic nature of bismuth is evident from the formation of electrovalent cations.

Hydrides of Arsenic, Antimony, and Bismuth. The compounds, *arsine*, AsH_3, *stibine*, SbH_3, and *bismuthine*, BiH_3, may be prepared by the reaction of the appropriate binary metal compound with water, a reaction of hydrolysis.

$$Zn_3As_2 + 6 \; HOH \longrightarrow 3 \; Zn(OH)_2 + 2 \; AsH_3$$
$$Mg_3Sb_2 + 6 \; HOH \longrightarrow 3 \; Mg(OH)_2 + 2 \; SbH_3$$
$$Mg_3Bi_2 + 6 \; HOH \longrightarrow 3 \; Mg(OH)_2 + 2 \; BiH_3$$
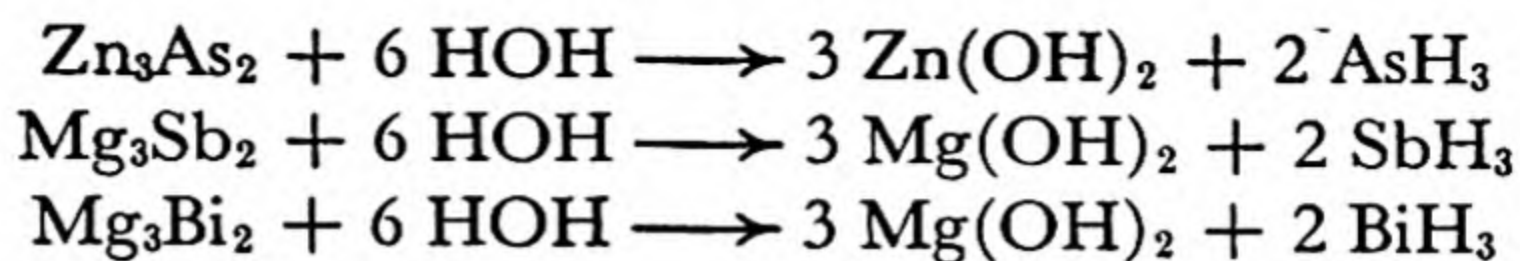
Arsine and stibine may also be formed by the reduction of arsenic and antimony compounds, respectively, by zinc in acidic solution.

$$[H_3AsO_4 + 8 \; H^+ + 8 \; \epsilon \longrightarrow AsH_3 + 4 \; H_2O] \times 1$$
$$\underline{[Zn \longrightarrow Zn^{++} + 2 \; \epsilon] \times 4}$$
$$H_3AsO_4 + 8 \; H^+ + 4 \; Zn \longrightarrow AsH_3 + 4 \; H_2O + 4 \; Zn^{++}$$
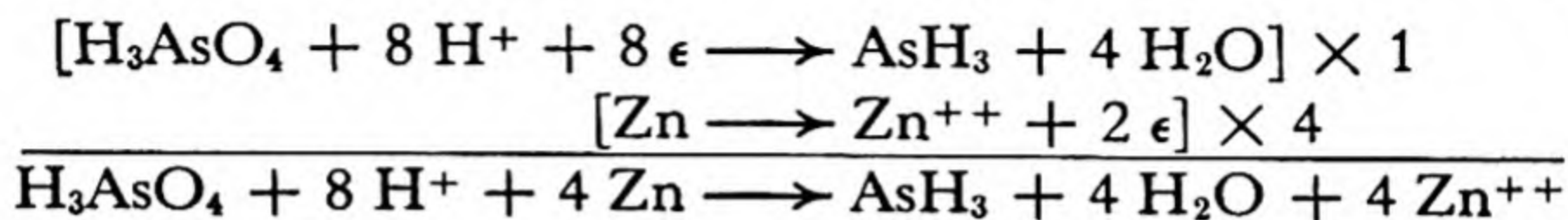
Arsine and stibine decompose when they are heated, and a deposit of arsenic or of antimony is obtained when a tube through which the gases are passing is heated. (Fig. 103.) Arsine burns with a lavender flame, forming water and arsenic trioxide.

Halides of Arsenic, Antimony, and Bismuth. These elements yield compounds in the 3 + state of oxidation with all of the halogens. They also produce halides in the 5 + state of oxidation, except for bismuth, which yields only

Fig. 103. Preparation of Arsine

the pentafluoride. The trichlorides are the most common of the halides. They may be prepared by direct union of the elements and by the reaction of the trioxides with concentrated hydrochloric acid. The other trihalides may be prepared by similar reactions.

These compounds undergo hydrolysis. The hydrolysis of phosphorus trichloride is irreversible because of the acidic nature of the hydroxide of phosphorus. The products of the reaction of arsenic trichloride with water are arsenious acid and hydrochloric acid. Arsenic trihydroxide is both weakly acidic and weakly basic. Hence, the reaction is reversible and equilibrium is established. The acidic properties of this substance are much more prominent than its basic properties, and the proportion of the trichloride at equilibrium is usually small.

$$AsCl_3 + 3 \; H_2O \rightleftharpoons H_3AsO_3 + 3 \; H_3^+ + 3 \; Cl^-$$
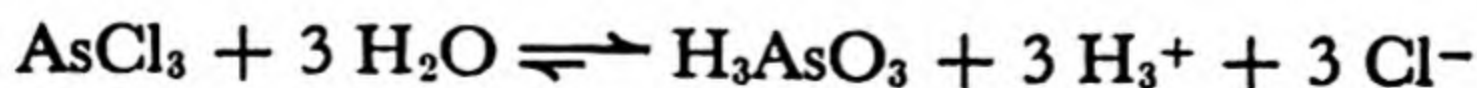
The hydrolysis of antimony trichloride is incomplete, producing at ordinary temperatures the slightly soluble antimonyl chloride and hydrochloric acid. The reaction is readily reversed by adding an excess of the acid.

$$Sb^{+++} + H_2O + Cl^- \rightleftharpoons SbOCl \downarrow + 2\,H^+$$
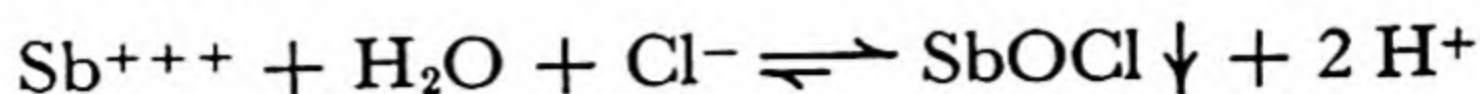
The hydrolysis of bismuth trichloride is similar to that of antimony trichloride.

$$Bi^{+++} + H_2O + Cl^- \rightleftharpoons BiOCl \downarrow + 2\,H^+$$
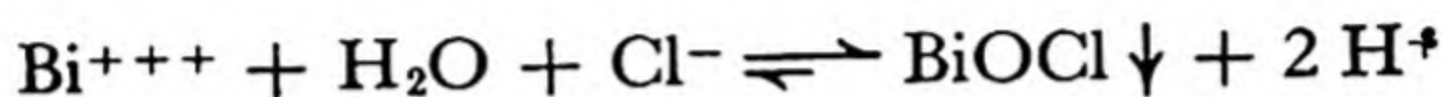
The reversibility of these reactions is due to the basic nature of the antimonyl and bismuthyl ions.

The Oxides and Hydroxides of Arsenic, Antimony, and Bismuth. These elements form oxides and hydroxides in their common oxidation states, 3 + and 5 +. There are also less important compounds in other oxidation states. The more common of these oxy-compounds are listed in Table 32.

TABLE 32. OXIDES AND HYDROXIDES OF ARSENIC, ANTIMONY, AND BISMUTH

Oxides	Arsenic	Antimony	Bismuth
Trioxide	As_2O_3	Sb_2O_3	Bi_2O_3
Pentoxide	As_2O_5	Sb_2O_5	Bi_2O_5
Acids			
Ortho, -ous	H_3AsO_3	H_3SbO_3	$Bi(OH)_3$
Meta, -ous	$HAsO_2$	$HSb(OH)_4$	—
Ortho, -ic	H_3AsO_4	—	—
Pyro, -ic	$H_4As_2O_7$	$HSb(OH)_6$	—
Meta, -ic	$HAsO_3$	—	$HBiO_3$

Oxides and Acids of Arsenic. Arsenic trioxide, As_2O_3, is formed when arsenic and its combustible compounds burn in air or in oxygen. This oxide, commonly called white arsenic, is obtained from flue dust in smelters. Many of the sulfide ores, especially copper sulfide ores, contain arsenic as an impurity, and the trioxide is formed when these ores are roasted. The oxide is resublimed and condensed to form a white solid. Arsenic trioxide is slightly soluble in water, reacting to form metarsenious acid as the usual product.

$$As_2O_3 \downarrow + H_2O \rightleftharpoons 2\,HAsO_2$$
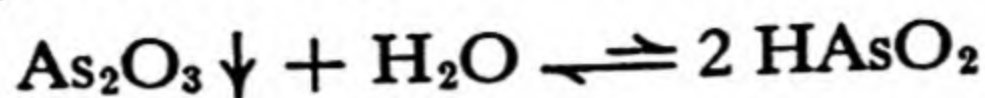
The oxide reacts with sodium hydroxide solution to produce both the metarsenite and the orthoarsenite.

$$As_2O_3 + 2\ OH^- \rightleftharpoons 2\ AsO_2^- + H_2O$$
$$As_2O_3 + 6\ OH^- \rightleftharpoons 2\ AsO_3^{---} + 3\ H_2O$$
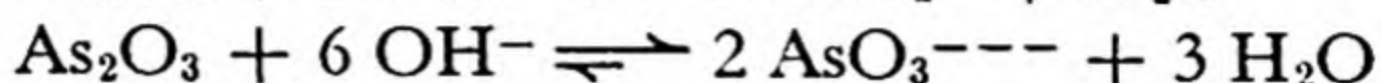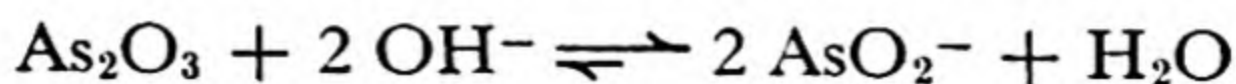
These ions are extensively hydrolyzed. Arsenic trioxide also exhibits weakly basic properties, reacting with concentrated hydrochloric acid to form the trichloride.

$$As_2O_3 + 6\ H^+ + 6\ Cl^- \rightleftharpoons 2\ AsCl_3 + 3\ H_2O$$
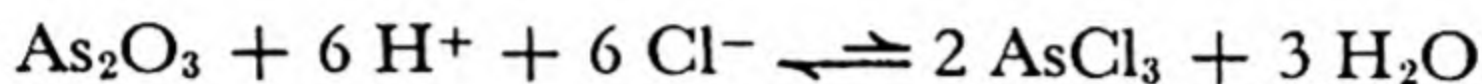
The trichloride is completely hydrolyzed in dilute solution.

Arsenic acid, H_3AsO_4, is formed by oxidation of arsenic trioxide by strong oxidizing agents such as hypochlorous acid and nitric acid.

$$[HClO + H^+ + 2\ \epsilon \longrightarrow Cl^- + H_2O] \times 2$$
$$\underline{As_2O_3 + 5\ H_2O \longrightarrow 2\ H_3AsO_4 + 4\ H^+ + 4\ \epsilon}$$
$$2\ HClO + As_2O_3 + 3\ H_2O \longrightarrow 2\ Cl^- + 2\ H^+ + 2\ H_3AsO_4$$
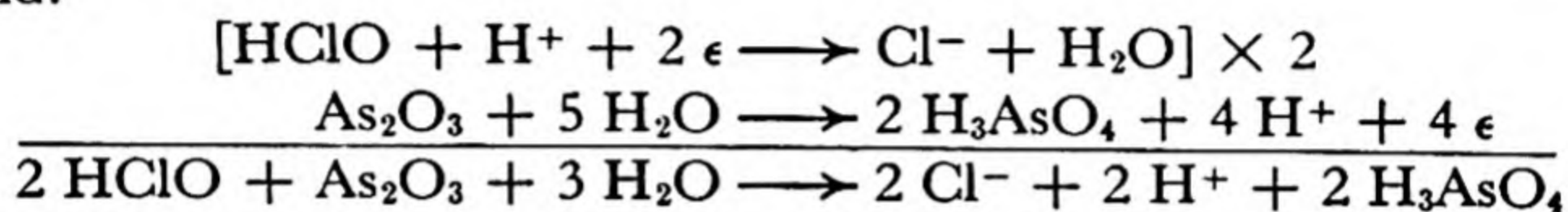
Arsenic acid is unstable toward heat, decomposing to yield successively pyroarsenic acid, metarsenic acid, arsenic pentoxide, and arsenic trioxide.

The most extensive uses of arsenic compounds are based on their action as poisons. More than one half of the arsenic trioxide produced is used in the preparation of insecticides, *e.g., Paris green,* a double salt consisting of copper acetate and copper arsenite, $Cu_4(C_2H_3O_2)_2(AsO_3)_2$, and *lead arsenate,* a mixture of the normal salt, $Pb_3(AsO_4)_2$, and the hydroarsenate, $PbHAsO_4$. Some of the chemical warfare agents, commonly called poison gases, are arsenic compounds, *e.g., Lewisite.* A number of organic arsenic compounds have medicinal uses, *e.g.,* salvarsan used in the treatment of syphilis. Arsenic trioxide is used in the production of weed-killing materials such as sodium arsenite. This oxide is also used in the glass industry.

Oxides and Acids of Antimony. Antimony trioxide, Sb_2O_3, may be formed by the direct union of antimony and oxygen and by the decomposition of the trihydroxide. This oxide is both basic and acidic. Consequently, it reacts with strong acids and with strong bases to form soluble compounds. Employing simplified formulas, the equations for the reactions are:

$$Sb_2O_3 + 6\ H^+ \longrightarrow 2\ Sb^{+++} + 3\ H_2O$$
$$Sb_2O_3 + 2\ OH^- + 3\ H_2O \longrightarrow 2\ Sb(OH)_4^-$$
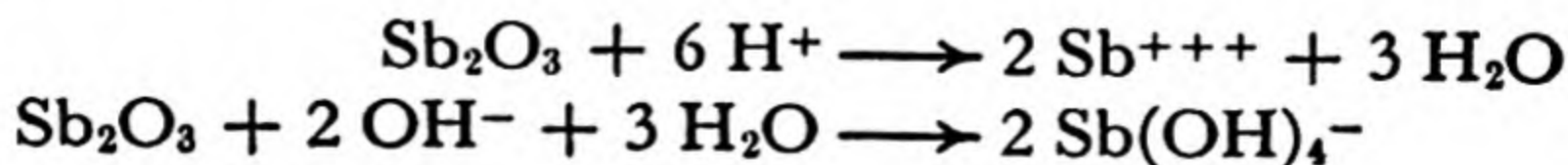
Antimony trihydroxide is an ampholyte, reacting with strong acids to form antimony salts and with strong bases to form antimonites.

$$Sb(OH)_3 + 3 H^+ \rightleftharpoons Sb^{+++} + 3 H_2O$$
$$Sb(OH)_3 + OH^- \rightleftharpoons Sb(OH)_4^-$$
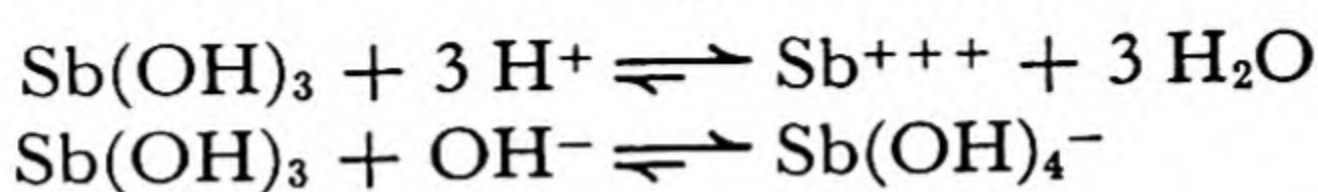
The antimony salts hydrolyze when dissolved in water, because of the weak acidic and basic properties of the trihydroxide. The antimony ion is almost completely hydrolyzed by hot water to form the antimonyl ion, SbO^+.

$$Sb^{+++} + H_2O \rightleftharpoons SbO^+ + 2 H^+$$
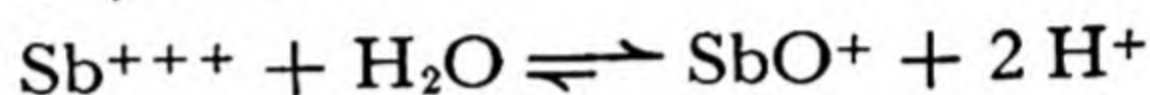
Antimonyl salts, such as the sulfate, $(SbO)_2SO_4$, and the nitrate, $SbONO_3$, may be crystallized from solution. Potassium antimonyl tartrate, $KSbOC_4H_4O_6$, has long been used in medicine as tartar emetic.

Antimonic acid is formed by the oxidation of the metal by nitric acid. It is slightly soluble and separates as a white precipitate having the composition $HSb(OH)_6$, or $HSbO_3(H_2O)_3$. The pentoxide may be formed by the decomposition of this acid. Both the oxide and the acid react with strongly basic solutions to form salts, *e.g.*, potassium pyroantimonate $KSb(OH)_6$.

$$Sb_2O_5 + 2 KOH + 5 H_2O \longrightarrow 2 KSb(OH)_6$$
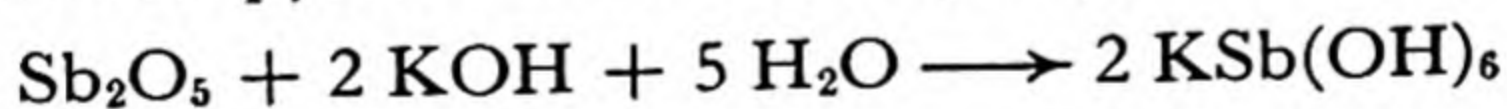
These salts are called pyroantimonates, but the composition is that of a metantimonate. The potassium salt is soluble in water, but the sodium salt has low solubility.

Oxides and Hydroxides of Bismuth. *Bismuth trioxide*, Bi_2O_3, occurs as a natural substance and may be prepared by the reaction of the metal with oxygen, by the roasting of the sulfide, and by the decomposition of the hydroxide. The trihydroxide is prepared by the reaction of soluble bismuth salts with basic solutions.

$$Bi^{+++} + 3 OH^- \rightleftharpoons Bi(OH)_3 \downarrow$$

The oxide and hydroxide are basic in properties

$$Bi_2O_3 + 6 H^+ \longrightarrow 2 Bi^{+++} + 3 H_2O$$
$$Bi(OH)_3 + 3 H^+ \longrightarrow Bi^{+++} + 3 H_2O$$
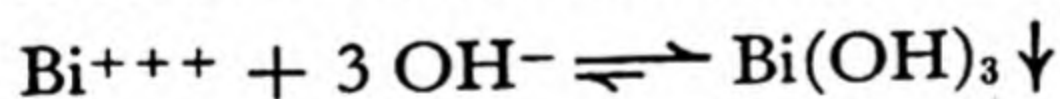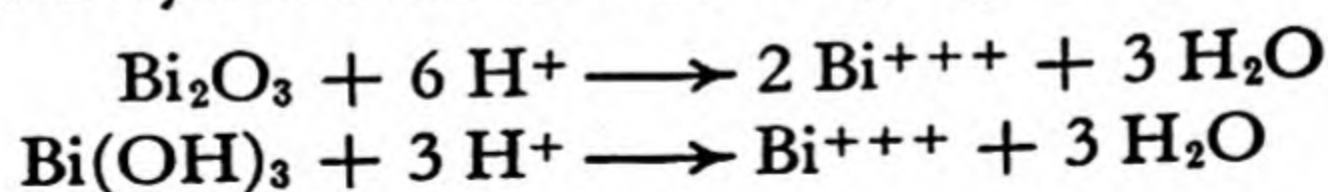
The trihydroxide does not exhibit acidic properties.

Bismuth ions hydrolyze to form bismuthyl ions, BiO^+, unless an excess of acid is present in the solution.

$$Bi^{+++} + H_2O \rightleftharpoons BiO^+ + 2\,H^+$$
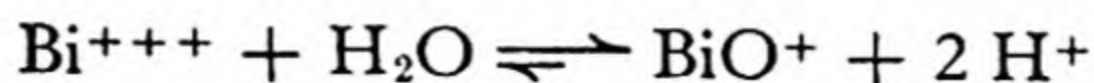
Bismuthyl nitrate, $BiONO_3$, and bismuthyl carbonate, $(BiO)_2CO_3$, are used medicinally, especially for the treatment of infections in the intestinal tract. Bismuthyl ions are readily reduced to the free metal. Bismuthyl hydroxide may be precipitated by the reaction of a solution of ammonia with a bismuth salt. The hydroxide is reduced, forming a jet black deposit of the metal, by reaction with a solution containing stannite ions, $Sn(OH)_4{}^{--}$, prepared by the reaction of an excess of a strong base with a stannous salt.

$$
\begin{array}{l}
[BiOOH + H_2O + 3\,\epsilon \longrightarrow Bi + 3\,OH^-] \times 2 \\
\underline{[Sn(OH)_4{}^{--} + 2\,OH^- \longrightarrow Sn(OH)_6{}^{--} + 2\,\epsilon] \times 3} \\
2\,BiOOH + 3\,Sn(OH)_4{}^{--} + 2\,H_2O \longrightarrow 2\,Bi + 3\,Sn(OH)_6{}^{--}
\end{array}
$$
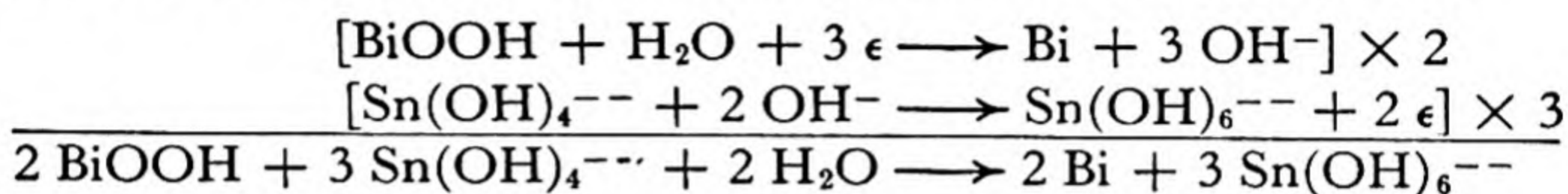
Bismuth pentoxide, Bi_2O_5, may be prepared by the oxidation of bismuth trioxide by strong oxidizing agents in weakly basic solution. The metabismuthate ion is formed is strongly basic solution.

$$
\begin{array}{l}
[ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-] \times 2 \\
\underline{Bi_2O_3 + 6\,OH^- \longrightarrow 2\,BiO_3{}^- + 3\,H_2O + 4\,\epsilon} \\
2\,ClO^- + Bi_2O_3 + 2\,OH^- \longrightarrow 2\,Cl^- + 2\,BiO_3{}^- + H_2O
\end{array}
$$
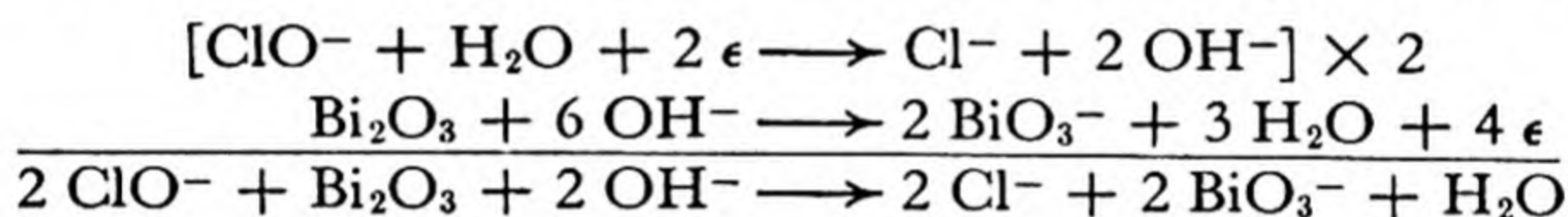
This substance is a strong oxidizing agent, oxidizing manganous compounds in acidic solution to permanganates.

$$
\begin{array}{l}
[BiO_3{}^- + 6\,H^+ + 2\,\epsilon \longrightarrow Bi^{+++} + 3\,H_2O] \times 5 \\
\underline{[Mn^{++} + 4\,H_2O \longrightarrow MnO_4{}^- + 8\,H^+ + 5\,\epsilon] \times 2} \\
5\,BiO_3{}^- + 2\,Mn^{++} + 14\,H^+ \longrightarrow 5\,Bi^{+++} + 2\,MnO_4{}^- + 7\,H_2O
\end{array}
$$
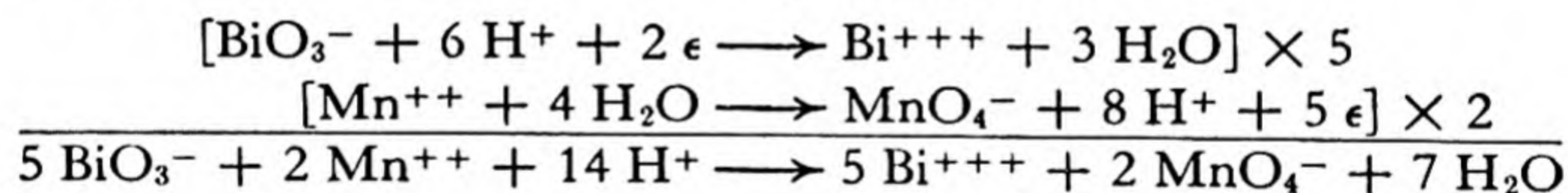
The Acid-Base Nature of the Hydroxides. The reactions discussed in this chapter illustrate a transition in the nature of the trihydroxides from distinctly acidic phosphorous acid, through weakly acidic arsenious acid and amphoteric antimony trihydroxide, to distinctly basic bismuth hydroxide. In terms of the electronic nature of the valence bonds, this is assumed to mean that the bond between oxygen and the member of this group becomes weaker as the atomic number becomes greater. Since all four of these elements have the same number of valence electrons, the molecules of these compounds have the same structural configurations, and the kernels of the atoms have the same net charge. The difference in behavior may be attributed to the greater size of the atoms with the

larger atomic numbers. The increased size of the atom not only decreases the attraction of the central atom of the cluster for the electron pairs constituting the bond with oxygen, but also decreases the repulsion of the proton in the hydroxide group and the activity of the compound in splitting off protons.

A second relationship noted among these compounds is that the hydroxide of each element in the high oxidation number is more acidic than in the lower state of oxidation. This effect would be expected to produce the opposite result to that discussed in the preceding paragraph. The polarity of the molecular hydroxide is increased by the introduction of additional oxygen atoms into the molecule. This results in an increased attraction of oxygen toward the central atom of the molecule, with a greater repulsion of the proton in the hydroxide group. This leads to an increased activity in splitting off protons.

Sulfides of Arsenic, Antimony, and Bismuth. Trisulfides of all three elements and pentasulfides of arsenic and antimony may be formed by direct union of the elements. They may also be prepared by precipitation. These sulfides are only slightly soluble and, consequently, may be precipitated by low concentration of sulfide ions obtained by passing hydrogen sulfide into acidic solutions.

$$2\,AsCl_3 + 3\,H_2S \rightleftharpoons As_2S_3 + 6\,H^+ + 6\,Cl^-$$

Arsenic trisulfide is yellow; antimony trisulfide, orange red; and bismuth trisulfide, black.

Thio Salts of Arsenic and Antimony. Thio salts of arsenic and antimony may be produced in both of the common oxidation states, $3+$ and $5+$, e.g., sodium thioarsenite, Na_3AsS_3, and sodium thioarsenate, Na_3AsS_4. The thio salts contain atoms of sulfur in place of the atoms of oxygen in ordinary salts. These salts are soluble and their formation reduces the concentrations of the ions of arsenic and antimony sufficiently to cause the sulfides to dissolve.

EXERCISES

1. Describe the production of each of the elements of the phosphorus family from natural materials.
2. Discuss the uses of the elements in this family.

3. Write equations to represent the reactions of these elements with each of the following: oxygen, sulfur, chlorine, and magnesium.

4. What methods may be used for the preparation of the hydrides of these elements? Illustrate by equations.

5. Compare the reactions of the halides of the members of the phosphorus family with respect to (a) methods of preparation, and (b) reactions with water. What do these reactions indicate concerning the metallic and nonmetallic nature of these elements?

6. What methods are used for the production of phosphoric acid?

7. Represent by equations three reactions of sodium hydroxide with phosphoric acid.

8. Show by equations the effect of heating hydrophosphates. Account for the fact that fused metaphosphates and pyrophosphates react with basic oxides, and illustrate the reactions by equations.

9. Discuss the use of phosphates in fertilizers. What three methods may be employed for the production of suitable fertilizer materials from insoluble phosphate rock.

10. Represent by equations the reactions of the elements of the phosphorus family with nitric acid.

11. Compare the trihydroxides of the elements of the phosphorus family in their behavior with hydrochloric acid and with sodium hydroxide. Illustrate by equations.

12. What transition in properties is observed among these elements in regard to (a) the nature of the ions which they form, (b) the products of hydrolysis of the trichlorides, and (c) the acid-base nature of the trihydroxides.

13. In terms of the electronic nature of their valence bonds, explain the increased basicity of the hydroxides of these elements with the increase in atomic number.

14. Explain the greater acidity of the hydroxide of an element in its higher oxidation numbers as compared to lower oxidation numbers.

SUPPLEMENTARY READINGS

Weeks, M. E., *The Discovery of the Elements*, Journal of Chemical Education, Easton, Pa., 1935, pp. 9–19; 345–53.

Riegel, R. E., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 7–8.

Landis, W. S., "Concentrated Fertilizers," *Ind. Eng. Chem.* 28, 1470 (1936).

McBride, R. S., "Fertilizer Practice at Curtis Bay," *Chem. Met. Eng.* 47, 1, 4 (1940).

Crass, M. F. Jr., "A History of the Match Industry," *J. Chem. Education* 18, 116, 277, 316, 380, 428 (1941).

"Superphosphate Production," Pictured Flow Sheet, *Chem. Met. Eng.* 50, 4, 132 (1943).

Chapter 23

CARBON. SILICON. BORON

Carbon and *silicon* are the first two members of Group IV of the periodic system. This group includes also *germanium, tin,* and *lead.* A transition in properties from nonmetal to metal is observed among the elements of this group as in the phosphorus family discussed in the preceding chapter. Carbon and silicon are definitely nonmetallic in properties, germanium is intermediate, and tin and lead are primarily metallic. The discussion of germanium, tin and lead is deferred to Chapter 29, where they are treated in connection with other metallic elements.

Although *boron* is the first member of Group III of the periodic system, it is included in this chapter, along with carbon and silicon, because of its weakly nonmetallic properties and its similarity to silicon.

CARBON

Carbon is a constituent of many compounds of varying complexity. Most of the substances produced by living organisms are carbon compounds. For a long time it was believed that these compounds could be formed only as the result of life processes, and for this reason, they were called *organic compounds.* Now a large number of carbon compounds may be synthesized from elementary substances and from simpler compounds. The organic compounds are composed chiefly of carbon, hydrogen, and oxygen, but nitrogen, phosphorus, the halogens, sulfur, and several other elements are constituents of a number of such compounds. The reactions of the organic compounds are molecular rather than ionic processes, and the systematic classification of these substances is based on other considerations than those employed for salts, acids, and bases. A few members of some simpler classes of organic compounds are discussed in the last two chapters of this text.

Occurrence of Carbon. Carbon occurs in elementary condition in coal and as diamond and graphite. Carbon dioxide is found in small and varying percentages in the atmosphere, and its salts, the carbonates, are widely distributed. The most common of these salts occur in *limestone* and *marble*, which are composed chiefly of *calcium carbonate*, $CaCO_3$, and *dolomite*, $CaCO_3MgCO_3$. Petroleum and natural gas are mixtures of carbon compounds, chiefly hydrocarbons. There are also many other carbon compounds of organic origin, such as alcohols, fats, carbohydrates, and proteins.

Allotropes of Carbon. Carbon exists in two distinctly different forms, diamond and graphite. The *diamond* crystal is usually octahedral in shape. In this crystal, each carbon atom is surrounded by four other atoms at the corners of a regular tetrahedron. Diamond is the hardest known substance. The specific gravity of the diamond is 3.5 at 20°, and it begins to volatilize at about 3500°. Diamonds have a high index of refraction, and the gems are cut so as to form facets which give maximum brilliance. Diamonds that are worthless as gems because of imperfections are used, because of their hardness, in cutting glass and as tips of drills. Diamonds are obtained chiefly from South Africa and Brazil. The largest diamond, the famous Cullinan, weighed 3032 carats or 606.4 g. Small diamonds were made by Moissan in 1894, by suddenly cooling a solution of carbon in melted iron. Under the conditions of temperature and pressure existing within the mass, carbon separates from the iron in the form of minute diamonds, but diamonds prepared in this way are too small to have any practical value.

Graphite consists of leaf-like crystals, between which there is but slight friction. It is soft and has a specific gravity of only 2.25. Graphite is used in the preparation of different lubricants. Mixtures of graphite and clay are used in making pencils, the hardness of the pencil depending on the proportions of the substances in the mixture. Graphite does not combine readily with oxygen and is used in stove polishes, and graphite crucibles are employed in certain high temperature reactions. Graphite is a fairly good conductor of electricity and is used in electrodes for arc lights and electric furnaces.

Graphite occurs in deposits in Ceylon, Siberia, and Madagascar.

Graphite is the product formed by the condensation of carbon vapor. Acheson's process for the production of graphite consists in passing an electric current through anthracite coal or coke, containing a small proportion of sand. The resistance to the passage of the current generates a large amount of heat, and at the high temperature carbon in the coal is changed to graphite.

Chars are involatile products of the decomposition of certain carbon compounds. Charcoal is produced from wood by destructive distillation and coke from coal. Pulverized carbon mixed with calcium phosphate is formed by the destructive distillation of bones. Boneblack is left as a residue when the calcium phosphate is dissolved from this mixture by reaction with hydrochloric acid. Carbon in the chars is commonly called *amorphous*, but examination by X-ray methods shows that it has a crystal structure similar to graphite. The chars are very porous and give a large surface area relative to the mass of material. Some of the chars have the property of adsorbing other substances to a high degree. (See page 134.) Because of this property, boneblack is used in the purification of cane sugar solutions, and some forms of carbon, such as cocoanut charcoal, are used in the canisters of gas masks. Charcoal may be activated by heating it in steam for a long time to remove adsorbed substances as completely as possible. Coke is extensively used as a fuel and as a reducing agent, particularly in the production of metals from their ores.

Carbon black is obtained as a sooty deposit when a smoky gas flame is cooled. A similar deposit may be obtained from the flame of burning oil. Large quantities of natural gas are burned annually to produce carbon black by causing the flame to impinge on a cold metal surface. A large proportion of the carbon black produced commercially is used in the rubber industry to increase the toughness of rubber and thus improve the product for automobile tires. Carbon black is also used in the production of ink and paint.

Reactions of Carbon. Carbon does not exhibit either positive or negative electrovalent states. Its reactions involve electron sharing in the formation of covalent bonds. In many instances these bonds are nonpolar. Not only does carbon yield a large number of compounds in which electrons are shared by carbon atoms and atoms of other elements, but also many compounds in which electrons

are shared between atoms of carbon, thus building up complex molecules of high molecular weight.

Carbon is not active at ordinary temperatures, but exhibits a number of important reactions at high temperatures. The reaction of carbon with oxygen is highly exothermic, and the combination of oxygen with carbon and carbon compounds furnishes the greater portion of the energy used in industrial operations. Graphite oxidizes only slowly at high temperatures, and diamonds must be heated to 800° to burn in oxygen. Depending on the proportions of available oxygen in contact with the burning material, the product is carbon monoxide or carbon dioxide.

$$2\,C + O_2 \longrightarrow 2\,CO + 52,860 \text{ cal.}$$
$$C + O_2 \longrightarrow CO_2 + 94,390 \text{ cal.}$$
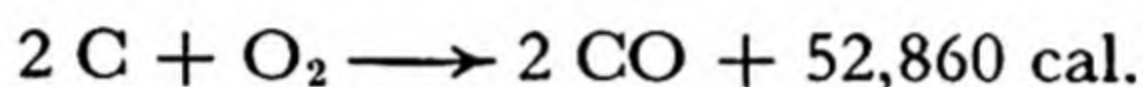
Hot carbon is an excellent reducing agent, and coke is the most extensively used reducing agent for the liberation of metals from their oxide ores.

$$ZnO + C \longrightarrow Zn + CO$$
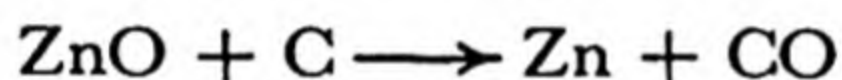
Carbon combines with many metals and with a few nonmetals, e.g., sulfur and silicon.

$$Ca + 2\,C \longrightarrow CaC_2$$
$$C + 2\,S \longrightarrow CS_2$$
$$C + Si \longrightarrow SiC$$
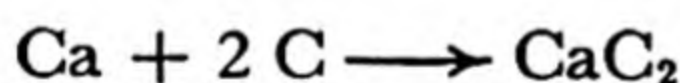
Carbon Dioxide. CO_2. Carbon dioxide in air, and the approximate balance between natural processes liberating this substance and those converting it into compounds have been discussed on page 48.

Preparation of Carbon Dioxide. There are a number of reactions that produce carbon dioxide. The most convenient laboratory method for the production of this gas is based on the reaction of an acid with calcium carbonate.

$$CaCO_3 + 2\,H^+ \longrightarrow Ca^{++} + H_2O + CO_2 \uparrow$$
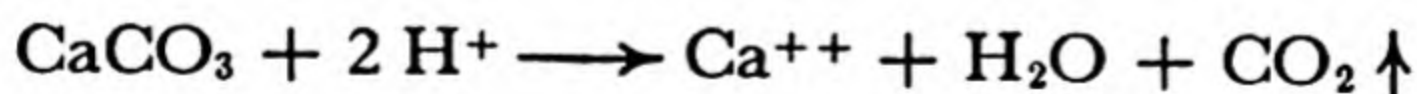
The gas may be collected by upward displacement of air. The industrial preparation of carbon dioxide is accomplished by the combustion of coke, the decomposition of calcium carbonate by

heat, and the fermentation of carbohydrates, such as dextrose, under the influence of enzymes.

$$C + O_2 \longrightarrow CO_2$$
$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$
$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2 \uparrow$$
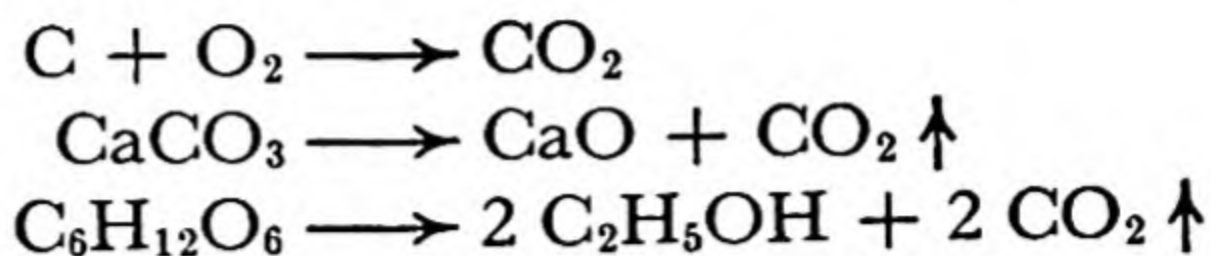
Carbon dioxide may be concentrated and separated from other gases by absorption in a solution of potassium carbonate under pressure, forming potassium hydrogen carbonate.

$$CO_3{}^{--} + H_2O + CO_2 \rightleftharpoons 2\,HCO_3{}^-$$
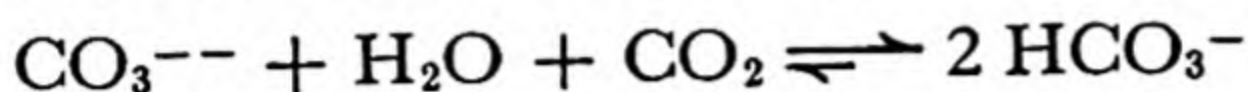
When the conversion to the hydrogen carbonate is complete, the pressure is reduced, and the solution is heated. As a result, the reverse reaction takes place, and carbon dioxide is evolved. The gas may be used directly, or may be dried, liquefied, and stored in cylinders for transportation and use elsewhere.

Properties of Carbon Dioxide. Carbon dioxide is a colorless and odorless gas. Its solubility in water at 25° and a gas pressure of one atmosphere is 0.145 g. in 100 g. of water. Carbonated water is a solution of the gas under a pressure of 3 or 4 atmospheres. The critical temperature of carbon dioxide is 31.55°, and the critical pressure is 73 atmospheres. The vapor pressure of the liquid is 59 atmospheres at 20°. Rapid evaporation occurs when the liquid is allowed to flow from a cylinder. The heat of vaporization is sufficiently great to freeze some of the liquid to a snowlike solid. This solid has a vapor pressure of one atmosphere at − 78.5°, and the solid sublimes.

Reactions of Carbon Dioxide. Carbon dioxide is stable toward heat and toward reduction at temperatures below 500°. It is decomposed to the extent of 2 per cent at 2000° and a pressure of one atmosphere.

$$2\,CO_2 \rightleftharpoons 2\,CO + O_2$$
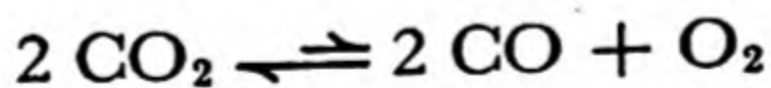
Active reducing agents reduce carbon dioxide at high temperatures. Magnesium will burn in an atmosphere of carbon dioxide, with the formation of magnesium oxide and elementary carbon.

$$2\,Mg + CO_2 \longrightarrow 2\,MgO + C$$
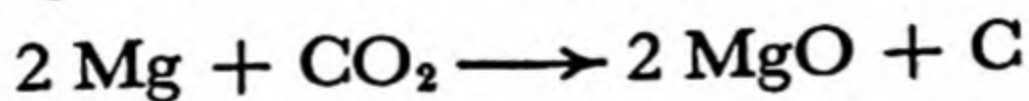
Carbon dioxide is reduced to the extent of about 94 per cent by an excess of carbon at 1000°.

$$CO_2 + C \rightleftharpoons 2\,CO$$

The percentage of carbon dioxide reduced by carbon at temperatures below 300° is small.

Carbon dioxide is an acidic oxide, forming weakly acidic solutions in water.

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$
$$\frac{[H^+] \times [HCO_3^-]}{[CO_2]} = 4.3 \times 10^{-7}$$
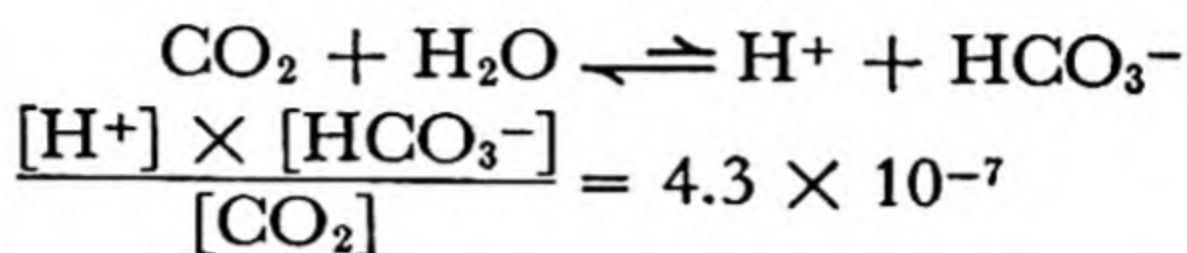
Carbon dioxide reacts with solutions of basic hydroxides to form carbonates. With an excess of carbon dioxide the hydrocarbonate is produced.

$$2\,OH^- + CO_2 \rightleftharpoons CO_3^{--} + H_2O$$
$$CO_3^{--} + H_2O + CO_2 \rightleftharpoons 2\,HCO_3^-$$
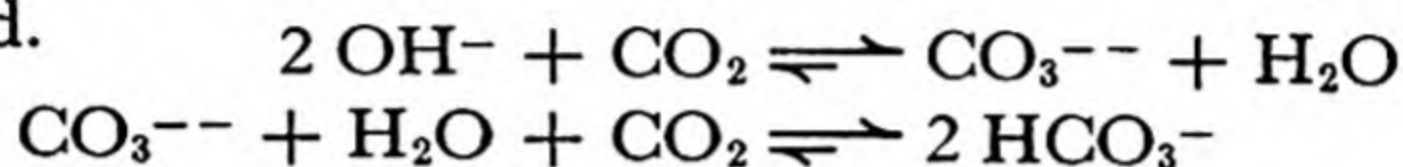
Carbon dioxide also reacts with active metal oxides to form carbonates.

$$CaO + CO_2 \rightleftharpoons CaCO_3$$
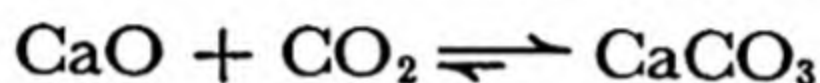
Uses of Carbon Dioxide. Carbon dioxide is extensively used in the preparation of soft drinks, in the production of sodium bicarbonate, sodium carbonate, and basic lead carbonate. The substance does not burn or support combustion, and is used therefore in the manufacture of fire extinguishers. One type contains sodium hydrogen carbonate and a bottle of sulfuric acid. (Fig. 104.) When the tank is inverted, the acid pours into the carbonate solution, and the reaction causes the water to become saturated with carbon dioxide. The excess of the gas rises to the top of the tank and creates a pressure which forces the solution out through the nozzle. The carbon dioxide carried by the solution mixes with the air surrounding the fire and reduces the con-

Fig. 104. Fire Extinguisher

centration of oxygen below that needed for combustion. In some fire extinguishers of this type, aluminum sulfate serves as the acid, and aluminum hydroxide is formed as a gelatinous precipitate.

$$Al(H_2O)_6^{+++} + 3\,HCO_3^- \longrightarrow Al(H_2O)_3(OH)_3\downarrow + 3\,H_2O + 3\,CO_2\uparrow$$

A foam of carbon dioxide and water, stabilized by the presence of aluminum hydroxide, is delivered through the nozzle. The addition of saponin to the solution further stabilizes the foam and aids in extinguishing the fire by blanketing it with an atmosphere of carbon dioxide.

Solid carbon dioxide is used as a refrigerant. Carbon dioxide snow, formed when the liquid evaporates rapidly, is compressed into large blocks, known as *dry ice*. Much lower temperatures may be maintained with this refrigerant than with water ice. The solid evaporates directly so that no liquid is formed, and the gas prevents the development of aerobic bacteria (bacteria which grow only in the presence of oxygen). For this reason dry ice is especially suited for use in the shipping of fruit and vegetables.

Carbonates. The carbonates are salts of carbonic acid, a weak and unstable acid existing only in solution in equilibrium with carbon dioxide. There are two series of salts corresponding to carbon dioxide, *viz.*, carbonates and hydrocarbonates, more familiarly known as *bicarbonates*. The normal salts, with the exception of the carbonates of sodium, potassium, and ammonium, have low solubility. The soluble carbonates may be prepared by the reaction of carbon dioxide with the appropriate soluble basic hydroxide, but are usually prepared by the special methods discussed in Chapter 25. The carbonates of low solubility are usually prepared by precipitation.

$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3 \downarrow$$
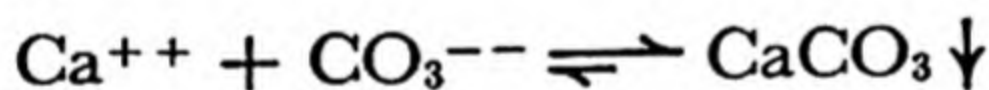
The hydrocarbonates are in general more soluble than the normal carbonates, with the exception of the salts of the alkali metals. They may be prepared by the reaction of water and carbon dioxide with the normal carbonates.

Reactions of the Carbonates. The carbonates react with an excess of an acid, forming carbon dioxide.

$$CaCO_3 \downarrow + 2 H^+ \longrightarrow Ca^{++} + H_2O + CO_2 \uparrow$$
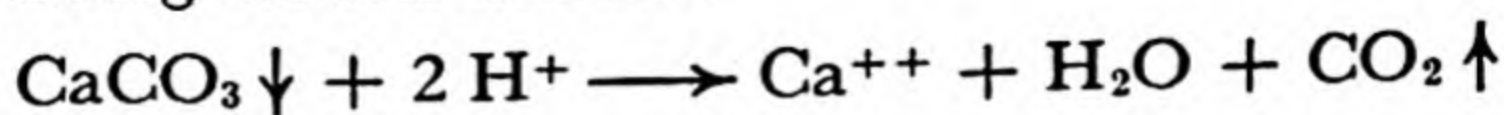
With low concentrations of hydrogen ions, from water and carbon dioxide or some other weak acid, the hydrocarbonate is produced.

$$CaCO_3 \downarrow + H_2O + CO_2 \rightleftharpoons Ca^{++} + 2 HCO_3^-$$
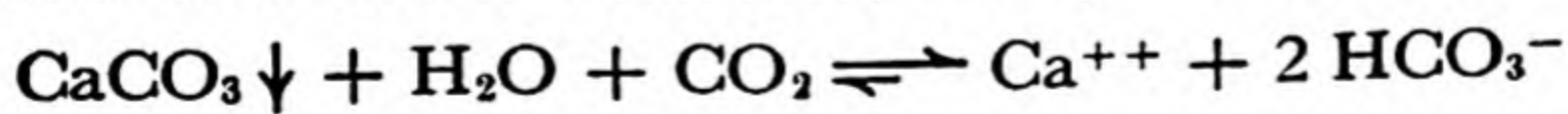
Most of the carbonates decompose when they are heated, with the

formation of carbon dioxide and the oxide of the metal. The carbonates of sodium and potassium, however, are stable toward heat. The carbonates react at elevated temperatures with most of the acidic oxides.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$
$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2 \uparrow$$
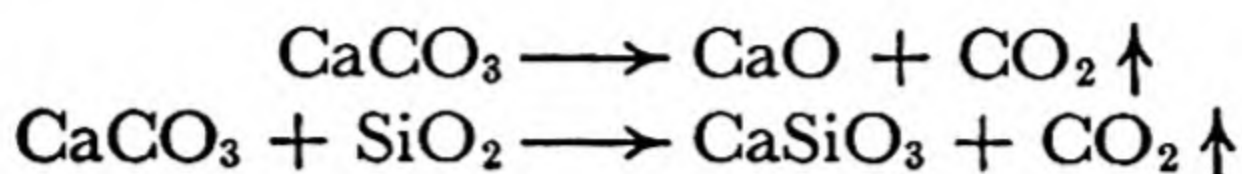
Bicarbonates are converted into carbonates by decreasing the concentration of hydrogen ions, thus causing a decrease in the concentration of the bicarbonate ion with a corresponding increase in the concentration of the carbonate ion. This result may be caused by the addition of basic substances. Calcium carbonate is precipitated by the reaction of calcium bicarbonate with calcium hydroxide.

$$Ca^{++} + HCO_3^- + OH^- \rightleftharpoons CaCO_3 \downarrow + H_2O$$
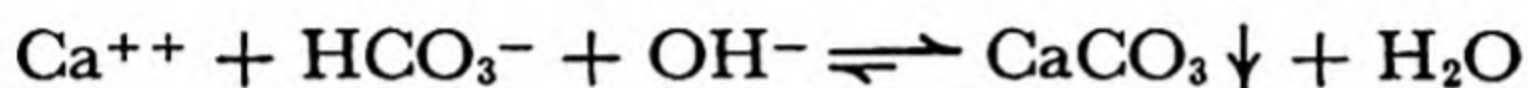
This reaction is virtually complete in basic solution, because the solubility product of calcium carbonate is small. Heating a solution of a bicarbonate produces the same result through the decomposition of the bicarbonate ion with the evolution of carbon dioxide.

$$2\,HCO_3^- \rightleftharpoons H_2O + CO_2 \uparrow + CO_3^{--}$$
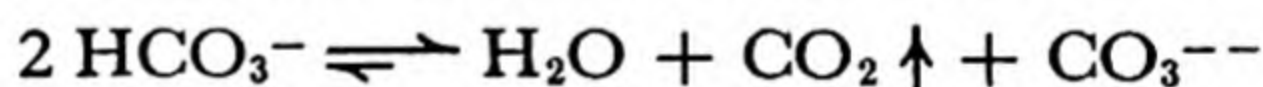
The concentration of carbonate ions is thus made great enough to cause the precipitation of calcium carbonate.

$$[Ca^{++}] \times [CO_3^{--}] > S_{CaCO_3} = 2 \times 10^{-8}$$
$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3 \downarrow$$
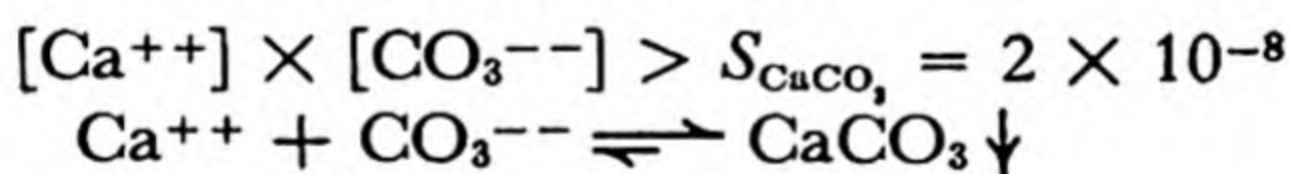
Soluble carbonates hydrolyze to form basic solutions, because of the basic nature of the carbonate ion.

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-$$
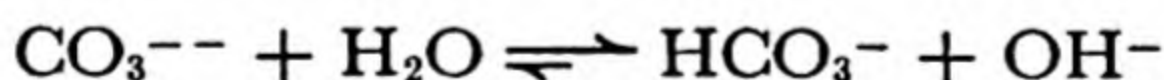
The presence of a carbonate in an unknown material is easily detected by its reaction with an acid to form carbon dioxide. The carbon dioxide is then passed into a solution of calcium hydroxide, forming a white precipitate of calcium carbonate.

$$CO_2 + Ca^{++} + 2\,OH^- \rightleftharpoons CaCO_3 \downarrow + H_2O$$
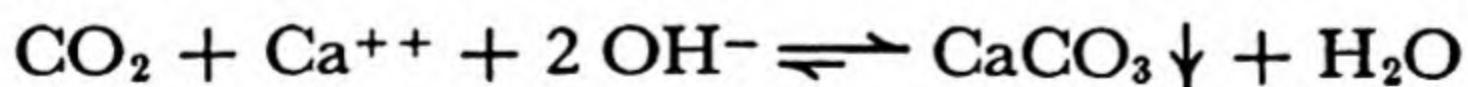
Acetic Acid. $HC_2H_3O_2$. Acetic acid, wood alcohol, and acetone are produced by the destructive distillation of wood. The condensed acid liquor, known as pyroligneous acid, is neutralized

with slaked lime, and solid calcium acetate is obtained by evaporation of the solution. Acetic acid is distilled from a mixture of this acetate and sulfuric acid.

$$Ca(C_2H_3O_2)_2 + H_2SO_4 \longrightarrow 2\,HC_2H_3O_2 + CaSO_4$$
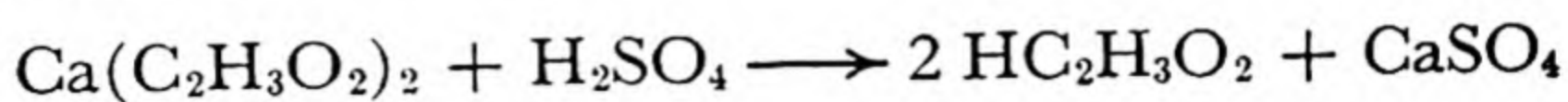
Acetic acid is also prepared by a synthetic process based on the reaction of acetylene with water to form acetaldehyde, which is then oxidized to acetic acid. Pure glacial acetic acid is a liquid that freezes at 16.7°. In aqueous solution it is a weak acid that finds extensive use in the laboratory. It is also used in the preparation of its salts and in the synthesis of a number of organic products, e.g., cellulose acetate, which is used in the manufacture of noninflammable film for photographic use and the manufacture of shatterproof glass.

Carbon Monoxide. CO. This oxide is the product of the incomplete combustion of carbon and carbon compounds. The amount of heat evolved when carbon burns to form the monoxide is only about one third as much as when carbon dioxide is produced. Therefore, the presence of carbon monoxide in the waste gases from burners and engines represents an economic loss. Carbon monoxide is formed by the reaction of steam with hot carbon.

Carbon monoxide resembles nitrogen in physical properties. The liquid boils at − 192°, freezes at − 207°, and has a critical temperature of − 139°. Carbon monoxide is very poisonous, combining with the haemoglobin to form a stable product that prevents combination of haemoglobin with oxygen. Carbon monoxide is not adsorbed to a significant degree in the gas masks prepared for use in air containing chemical warfare agents such as phosgene and mustard gas. It is oxidized to carbon dioxide by oxygen in contact with a mixture of the oxides of manganese and copper, known as *hopcalite*. Gas masks intended for use in an atmosphere contaminated by carbon monoxide are arranged so that the air is drawn through this catalyst.

Carbon monoxide reacts with many metals to form complex products known as *carbonyls*, e.g., iron carbonyl, $Fe(CO)_5$; nickel carbonyl, $Ni(CO)_4$; and cobalt carbonyl, $Co(CO)_4$. The formation of nickel carbonyl is an important step in one of the processes for the extraction of nickel from ores. Carbon monoxide also reacts

with chlorine in direct sunlight and in contact with activated charcoal to form *carbonyl chloride*, known as *phosgene*.

$$CO + Cl_2 \longrightarrow COCl_2$$
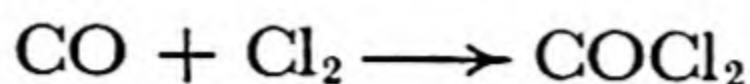
Phosgene is a colorless gas at room temperature. The boiling point of the liquid is 8.3°. It is a lung irritant and causes general collapse when breathed. It was used extensively as a poison gas during World War I.

Carbon Monoxide as a Fuel Gas. A number of combustible materials are important as fuels. For many purposes, gaseous fuels provide a more convenient source of heat than solids, because gas burners are usually more efficient in the utilization of fuel. Consequently, large quantities of gaseous fuels are produced from solid and liquid fuels for household and industrial use. Carbon monoxide is an important component of most of the manufactured fuel gases.

Producer gas is manufactured by the incomplete combustion of coal. Air is passed through a thick bed of coke or anthracite coal in a suitable furnace (Fig. 105) so that combustion occurs at the base. Carbon dioxide formed in this reaction rises

Fig. 105. Diagram of a Producer-Gas Plant

through the hot coke or coal and is reduced to carbon monoxide.

$$CO_2 + C \rightleftharpoons 2\,CO$$

The gas mixture produced in this manner contains approximately 40 per cent of combustible materials, largely carbon monoxide. The remaining 60 per cent is mainly nitrogen from the air blown through the hot solid fuel. The heating value of this fuel gas is relatively low, because of the large percentage of incombustible material.

Water gas is produced by the reaction of steam with coke or anthracite coal at high temperatures. Water gas contains approxi-

mately 50 per cent of hydrogen and 40–45 per cent of carbon monoxide, with small percentages of incombustible gases. The heating value of this gas is high. The industrial fuel gas is generally enriched with gaseous hydrocarbons produced by the destructive distillation of bituminous coal or by the decomposition of complex hydrocarbons in fuel oils.

Calcium Carbide. CaC_2. Calcium carbide is produced by heating calcium oxide and coke in an electric furnace at a temperature of about 3000°.

$$CaO + 3\,C \longrightarrow CaC_2 + CO$$
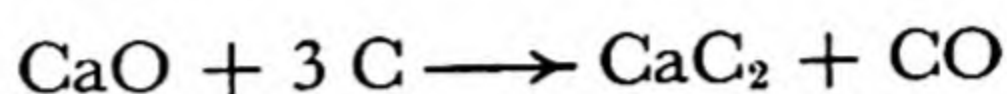
Calcium carbide reacts with water, forming *acetylene*, C_2H_2, which is important as a fuel gas in the oxyacetylene torch.

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
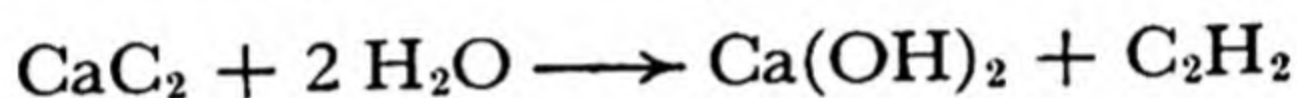
Calcium carbide also reacts with nitrogen, forming calcium cyanamide, one of the important reactions in nitrogen fixation. (See page 342.)

Silicon Carbide. SiC. This substance was discovered by Acheson in 1891, and was named *Carborundum* under the mistaken impression that it was a compound of carbon and corundum, an oxide of aluminum. Silicon carbide is now prepared in large quantities at Niagara Falls by the Acheson process. In an electric furnace, a current is passed through a mixture of sand and coke, containing varying amounts of sawdust and common salt. The reaction may be represented by the following equation.

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO \uparrow$$
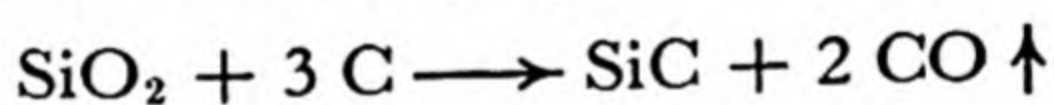
The sawdust is used to make the mixture porous, so that the carbon monoxide may pass through the charge and escape, and the salt reacts with iron compounds to form ferric chloride which is volatilized.

Carbon Disulfide. CS_2. This compound is prepared in an electric furnace by heating charcoal and sulfur in the absence of air.

$$C + 2\,S \longrightarrow CS_2$$
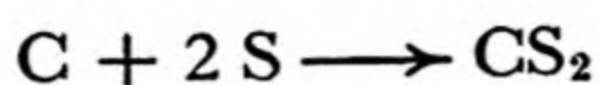
Carbon disulfide is a volatile liquid with a boiling point of 46.3°. Hence, the product is condensed as it emerges from the furnace

in the form of a gas. Carbon disulfide burns in air with the formation of carbon dioxide and sulfur dioxide.

$$CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2$$
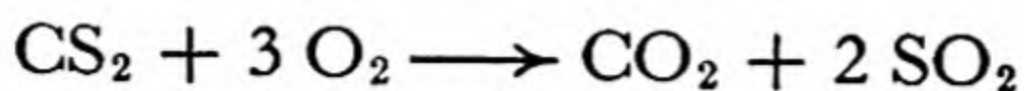
Mixtures of gaseous carbon disulfide and air may explode when ignited. Carbon disulfide is used as a solvent for fats, and for sulfur, phosphorus, and iodine. It is extensively used in the production of carbon tetrachloride. The vapor of carbon disulfide is poisonous, and the substance is used to kill rats, mice, prairie dogs, and ants.

Carbon Tetrachloride. CCl₄. Carbon tetrachloride may be prepared by the reaction of gaseous carbon disulfide with chlorine at high temperatures, and by passing chlorine into carbon disulfide containing iodine which serves as a catalyst.

$$CS_2 + 3\,Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$
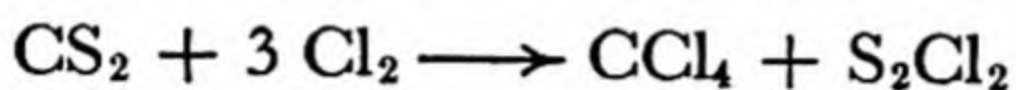
Both products are liquids, but carbon tetrachloride has the lower boiling point, 77°, and is separated by distillation from sulfur monochloride, which has a boiling point 136°. Carbon tetrachloride is a colorless liquid insoluble in water. It dissolves fats and tars readily and is used in extracting grease from wool and from oil-bearing seeds. It is noninflammable. Carbon tetrachloride is easily volatilized and forms a heavy vapor which does not support combustion. Under the name *pyrene* it is used in fire extinguishers.

SILICON

The element does not occur free in nature. Its important natural compounds are silica, in the form of sand and quartz, and silicates of varying degrees of complexity. Compounds of silicon make up about 87 per cent of the matter in the outer layer of the solid earth, and the element ranks next after oxygen in abundance.

Elementary Silicon. The element may be prepared in the form of very small crystals, commonly called amorphous silicon, by heating silicon dioxide with magnesium or the tetrachloride with sodium.

$$SiO_2 + 2\,Mg \longrightarrow Si + 2\,MgO$$
$$SiCl_4 + 4\,Na \longrightarrow Si + 4\,NaCl$$
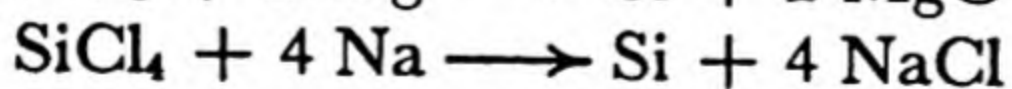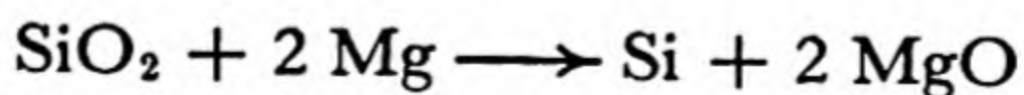
Silicon is prepared commercially by heating a mixture of sand and coke in an electric furnace, using a smaller proportion of coke than

in the production of silicon carbide. The most important uses of the element are in the steel industry, where ferrosilicon, composed primarily of compounds of iron with silicon, is commonly employed. Ferrosilicon is prepared by reducing a mixture of iron oxide and silica with carbon in an electric furnace. *Duriron*, which contains about 16 per cent of silicon, is an acid resistant metal. Ferrosilicon is added to melted steel to remove gas bubbles which would cause flaws.

The atoms of silicon contain four valence electrons, and the reactions of the element lead to the formation of covalent bonds. Silicon yields binary compounds with many of the metals, a few nonmetals, and with oxygen and hydrogen. There are also a number of complex compounds of silicon, chiefly the complex silicates.

Silicides of Metals. Silicides of the metals are formed by the direct union of the elements at high temperatures. When a mixture of powdered sand and an excess of magnesium powder is heated, a portion of the silicon formed by the reduction of the oxide combines with the excess of the magnesium to form the binary product, *magnesium silicide.*

$$SiO_2 + 2\,Mg \longrightarrow Si + 2\,MgO$$
$$Si + 2\,Mg \longrightarrow Mg_2Si$$
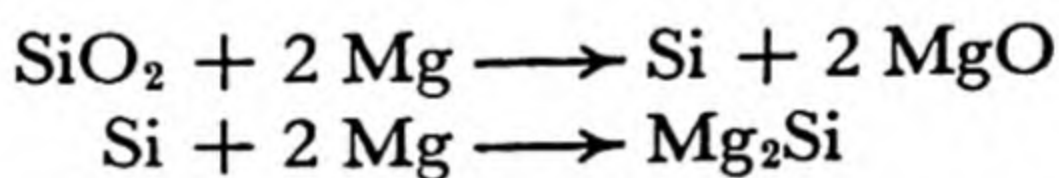
This compound does not exhibit the structure or the properties of a salt. It reacts with hydrochloric acid to form a mixture of hydrides of silicon, of which the simplest is silicomethane, SiH_4, which is analogous to methane, CH_4.

$$Mg_2Si + 4\,HCl \longrightarrow 2\,MgCl_2 + SiH_4$$
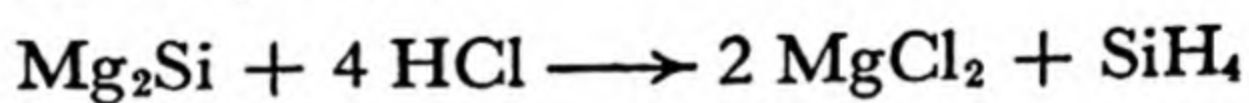
The hydrides of silicon are spontaneously combustible in air and burn with the formation of silicon dioxide and water.

$$SiH_4 + 2\,O_2 \longrightarrow SiO_2 + 2\,H_2O$$
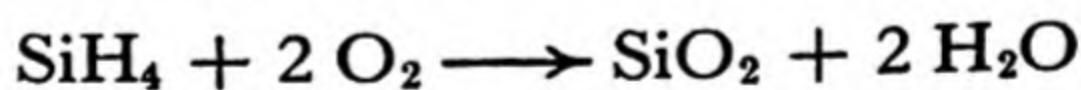
Halides of Silicon. Silicon unites directly with the halogens to form tetrahalides. Silicon ignites spontaneously in an atmosphere of fluorine, but must be heated to start the reaction with the other halogens. The stability of *silicon tetrafluoride*, SiF_4, is so great that silicon dioxide and most of the silicates react with hydrofluoric acid.

$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O$$
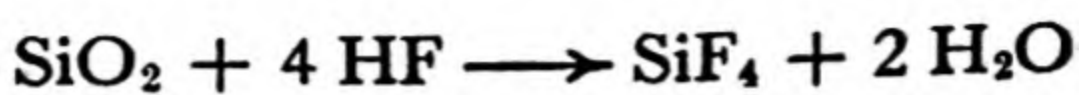
Silicon tetrafluoride is a gas at room temperatures. It hydrolyzes to form the weak silicic acid and the moderately strong fluosilicic acid.

$$3 SiF_4 + 3 H_2O \longrightarrow 2 H_2SiF_6 + H_2SiO_3$$
$$H_2SiF_6 + 2 H_2O \rightleftharpoons 2 H_3O^+ + SiF_6^{--}$$
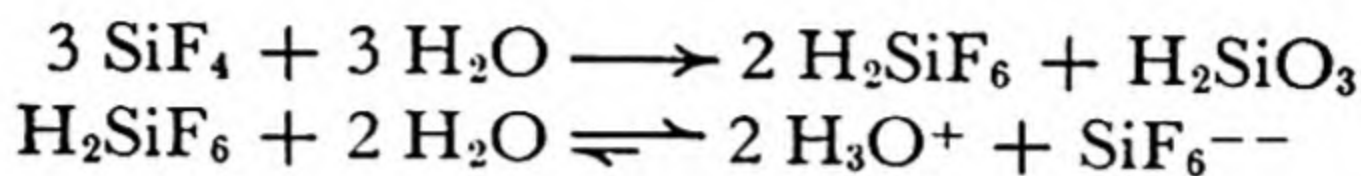
The potassium salt of this acid is only slightly soluble and the lead salt is highly soluble.

Silicon tetrachloride, $SiCl_4$, is prepared by the reaction of chlorine with a hot mixture of silica and carbon.

$$SiO_2 + 2 C + 2 Cl_2 \longrightarrow SiCl_4 + 2 CO$$
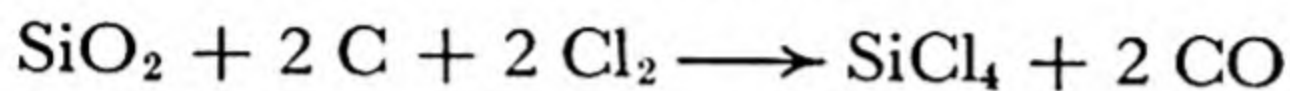
Silicon tetrachloride is a liquid which freezes at $-70°$ and boils at $57.6°$. It fumes strongly in moist air, because its hydrolysis produces hydrogen chloride and silicic acid or hydrated silica.

$$SiCl_4 + 3 H_2O \longrightarrow 4 HCl + H_2SiO_3$$
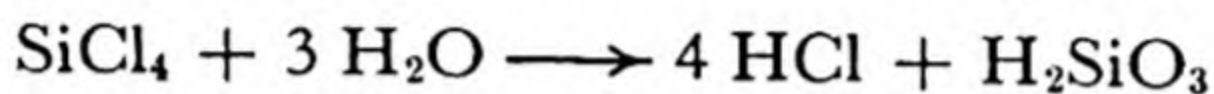
It is used to some extent in the production of smoke screens.

Silicon Dioxide. Silica. SiO_2. Silicon dioxide is common in the outer part of the earth. It exists in several crystalline modifications, quartz being the stable form at ordinary temperatures. Pure quartz is a clear colorless crystal, but silica often has color due to impurities, as in smoky quartz and rose quartz. Amethyst contains manganese, onyx, agate, and jasper contain iron, and opal and flint are composed of crystalline hydrated silica. Diatomaceous earth, used as a polishing powder, is finely divided silica which has been deposited by the disintegration of microscopic vegetable organisms.

Silicon dioxide is a very stable compound. Nevertheless, because of the formation of a surface layer of the oxide, silicon does not unite readily with oxygen. Silicon dioxide does not unite with water to form acids, but it does react with fused basic oxides and hydroxides to form orthosilicates and metasilicates.

$$SiO_2 + 2 NaOH \longrightarrow H_2O + Na_2SiO_3$$
$$SiO_2 + 4 NaOH \longrightarrow 2 H_2O + Na_4SiO_4$$
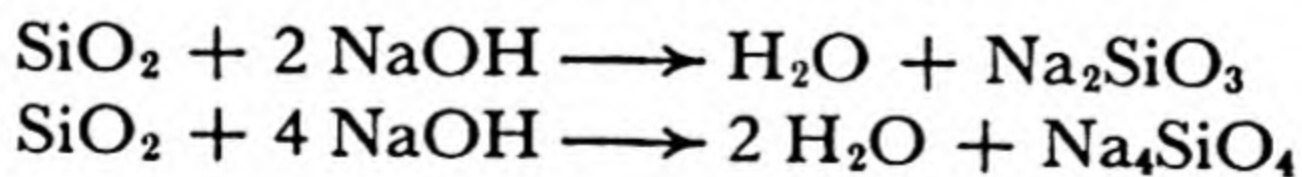
Many of the other nonmetal oxides are more volatile than silica, and, consequently, many salts react with silica at high temperatures. with the evolution of other acidic oxides.

$$Ca_3(PO_4)_2 + 3 SiO_2 \longrightarrow 3 CaSiO_3 + P_2O_5$$
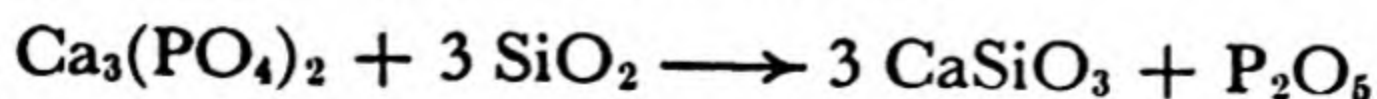
Crystalline forms of silica melt at about 1700° to form a viscous liquid. The liquid supercools without crystallization to form a product known as quartz glass. This product does not soften at temperatures below 1500°, while ordinary glass softens at temperatures of about 700° or 800°. Fused silica is used in making many forms of laboratory apparatus, e.g., combustion tubes, flasks, beakers, and crucibles. The coefficient of expansion of quartz glass is so low that it may be cooled suddenly from high temperatures without breaking. Quartz glass transmits ultraviolet light much more readily than ordinary glass. Hence, it is used in the manufacture of ultraviolet lights, certain types of optical instruments, and apparatus in which photochemical effects are investigated.

Silicic Acids. The addition of a strong acid to a solution of a soluble silicate results in the formation of a gelatinous precipitate of hydrated silica. When this product is strongly heated, water is driven out and dehydrated silicon dioxide is left as a residue. The partially dehydrated product, *silica gel*, adsorbs a number of substances to a high degree, and has many industrial uses based on this property.

Silicates. The salts corresponding to orthosilicic and metasilicic acids are simple silicates. There are also a number of salts in which the negative radical contains two or more atoms of silicon. These salts of hypothetical complex silicic acids occur extensively in nature. They are known as polysilicates.

The most abundant igneous rock, formed by the solidification of the molten matter of the earth, is granite. Granite is a mixture of quartz, feldspar, and mica. The common feldspar, *orthoclase*, is a complex silicate having the composition $KAlSi_3O_8$. The micas are salts of orthosilicic acid, containing aluminum and alkali metals, e.g., *muscovite*, $KAl_3H_2(SiO_4)_3$. *Talc* is a magnesium salt of metasilicic acid, $Mg_3H_2(SiO_3)_4$. The name *asbestos* is applied to several of the magnesium silicates. Kaolin or clay is an impure material containing *kaolinite*, $Al_2Si_2O_7(H_2O)_4$, a hydrated salt of one of the complex silicic acids. Many of the complex silicates have important uses, e.g., granite and sandstone as building materials, kaolin for the manufacture of brick and pottery, asbestos as a heat insulator, mica as an electrical insulator, talc in soap,

talcum powder, rubber, and roofing materials, beryl as an ore of beryllium, and many others.

The continued breathing of air containing the dust of silicate materials results in a pulmonary disease known as *silicosis*. This condition is frequently encountered among tunnel workers who have been drilling and blasting silicate rock.

Some of the natural silicates that are salts of orthosilicic acid or of metasilicic acid may be decomposed by hydrochloric acid, but many of the complex silicates cannot be decomposed by the common acids. Two methods are in general laboratory use for the decomposition of these materials. A mixture of simple silicates and oxides may be formed by fusing the complex silicate with sodium carbonate. This product may be decomposed by hydrochloric acid with the precipitation of hydrated silica. The complex silicates react with hydrofluoric acid, forming gaseous silicon tetrafluoride and the fluorides of the metals.

Soluble Silicates. The simple silicates of sodium and potassium are soluble in water. The other simple silicates have only low solubility in water. Both sodium metasilicate, Na_2SiO_3, and sodium orthosilicate, Na_4SiO_4, are prepared commercially for use in soap. These salts hydrolyze, producing strongly basic solutions. Consequently, they neutralize bicarbonates and cause the removal of ions, such as calcium and magnesium, often present in water in the form of the bicarbonate. Such compounds of calcium and magnesium react with soap to form insoluble products and thus cause a great waste of soap in laundry and household use.

A commercial product known as *water glass* is prepared by fusing powdered quartz with sodium carbonate and extracting the product with water. Water glass is also prepared by boiling a suspension of silica in a sodium hydroxide solution at a pressure of approximately 4 atmospheres to permit higher temperatures. The product is a syrupy liquid containing silicates of sodium in solution and finely divided silica in suspension. Water glass is used as fireproofing material, egg preservative, glue for cardboard boxes, sizing in paper, and a number of other purposes.

Glass. Glass is a noncrystalline product, formed by fusing sand and other nonmetal oxides with various basic substances. The product is a supercooled liquid solution of the different components

in each other at ordinary temperatures, and the composition may be varied, depending on the uses for which the glass is intended. Glass has no fixed melting point but gradually softens when it is heated.

The properties of glass differ, depending on its composition. Common *soda glass* contains silicates and silica in proportions equivalent to approximately 75 per cent of silica, 15 per cent of sodium oxide, and 10 per cent of calcium oxide. These proportions may be varied, and glass may also contain aluminum compounds. Soda glass is used in making bottles, window glass, glass tubing, and many other products. It is called *soft glass* because it softens enough to be shaped and worked at moderately low temperatures, such as those given by the flame of the Bunsen burner. *Potassium glass* contains potassium instead of sodium in the silicate. It softens at higher temperatures and is called *hard glass*. The potassium-lead glass, known as *flint glass*, has high density and reflects light to a high degree. It is used in making cut-glass objects and optical instruments. A glass composed of borates and silicates is made by the addition of boric oxide to the charge. *Pyrex* glass contains large percentages of acidic oxides, about 80 per cent of silicon dioxide and 12 per cent of boric oxide. It has a low coefficient of expansion and therefore is suitable for the manufacture of laboratory apparatus and ovenware.

Glass is annealed by passing it slowly through a furnace hot at one end and much cooler at the other. In this way the glass cools slowly and uniformly, and internal stresses are not developed or are relieved. In thick glass objects, the process of annealing may take a long time. The annealing of the 200-inch reflector for the great telescope at Mt. Palomar, California, required about one year.

The greatest demand for plate glass is now in the automobile industry. The danger of serious injury resulting from broken windows and flying glass has led to the development of shatterproof glass. Two layers of plate glass are cemented together with an intermediate layer of a plastic such as a Vinal resin. When this glass is broken, the fragments are held together by the central layer. Bulletproof windows are made in the same manner, through the use of five or more layers.

Glass bricks and tile are now used as construction materials in buildings. Finely divided glass fiber is extensively used in heat insulation of buildings and has limited uses as a textile fiber.

Portland Cement. Portland cement is prepared by heating a mixture of finely ground limestone and clay of the proper composition. The mixed materials are "burned" in a rotary kiln (Fig. 106), in which they gradually work down to the hot end,
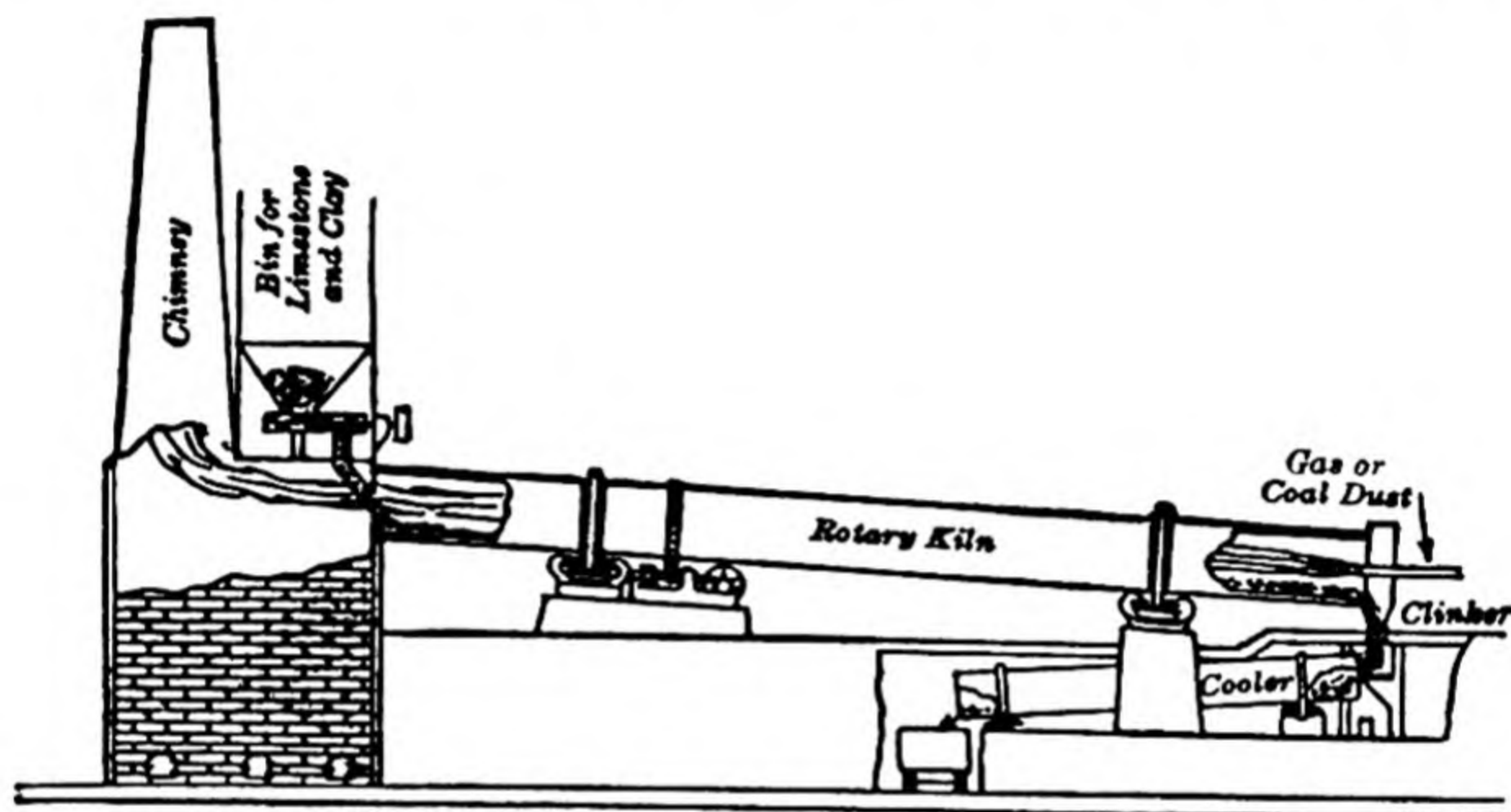
Fig. 106. Diagram of a Cement Kiln

where the temperature is 1400–1600°. At this temperature, the substances partially fuse and form lumps known as clinkers. After cooling, the product is ground with 2–3 per cent of gypsum. The product consists for the most part of three compounds, *viz.*, dicalcium silicate, Ca_2SiO_4; tricalcium silicate, Ca_3SiO_5; and calcium aluminate, $Ca_3(AlO_3)_2$. The setting of cement is due to the hydration of these compounds, and the rate of setting is regulated by the gypsum. Gelatinous products are first formed, and these gradually harden and cement the crystals together. The changes occurring during the hardening of cement are complex and continue for a long time. The first stages are complete in 28–30 hours. Cement is used primarily in a mixture with rock and sand to make concrete. The fact that it will set beneath the surface of water permits its use in building dams, piers for bridges, canal locks, and many other structures. The annual production of Portland cement in the United States is normally about 160,000,000 barrels.

BORON

Boron occurs among the natural substances to only a small extent. It is found in boric acid and borates. The acid is volatilized in steam issuing from the ground in Tuscany. Magnesium borate is found in salt deposits in Germany at Stassfurt. In the western part of the United States, deposits of *colemanite*, $Ca_2B_6O_{11}(H_2O)_5$, *borax*, $Na_2B_4O_7(H_2O)_{10}$, and *kernite*, $Na_2B_4O_7(H_2O)_4$, are found. These deposits were produced by long-continued evaporation of inland bodies of water. Borax is recovered from the brines of some of the lakes, such as Searles Lake. A binary compound with carbon, called *boron carbide*, B_4C, is formed when boric oxide is reduced by carbon in an electric furnace. This compound is a very hard solid, used in making dies for drawing wire and in jeweled bearings.

Boric Oxide and Boric Acid. Boric oxide is formed by strongly heating boric acid.

$$2\,H_3BO_3 \longrightarrow B_2O_3 + 3\,H_2O$$
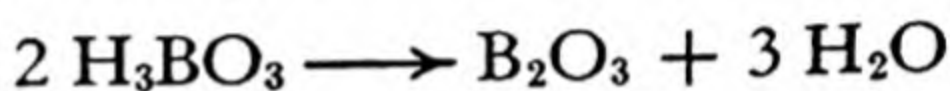
The product is a hard, brittle, glasslike solid at room temperature. Boric oxide reacts with basic oxides and hydroxides to form metaborates, salts of metaboric acid, HBO_2, when the substances are heated together.

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$$
$$2\,NaOH + B_2O_3 \longrightarrow 2\,NaBO_2 + H_2O$$
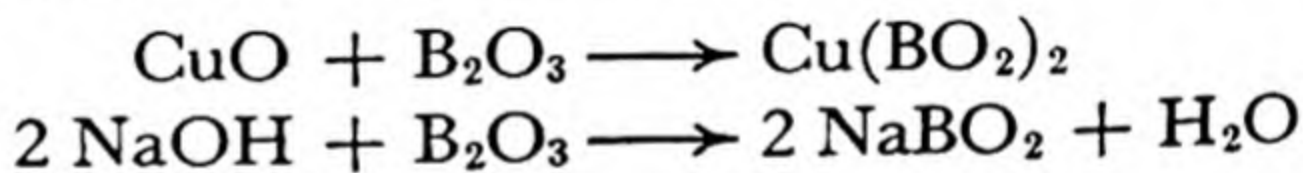
Boric acid is a weak acid, moderately soluble in cold water. The solubility increases greatly with rise in temperature, *e.g.*, 4.8 g. in 100 g. of water at 20°, 39.1 g. at 100°. Boric acid is usually prepared by the reaction of sulfuric acid with borax.

$$B_4O_7^{--} + 2\,H^+ + 5\,H_2O \longrightarrow 4\,H_3BO_3$$
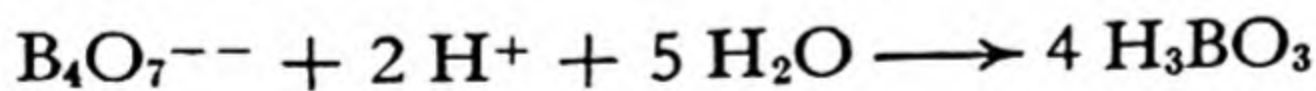
Boric acid is a mild antiseptic.

Boric acid is decomposed by heat with the formation of metaboric acid, tetraboric acid, and finally boric oxide.

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$
$$4\,HBO_2 \longrightarrow H_2B_4O_7 + H_2O$$
$$H_2B_4O_7 \longrightarrow 2\,B_2O_3 + H_2O$$
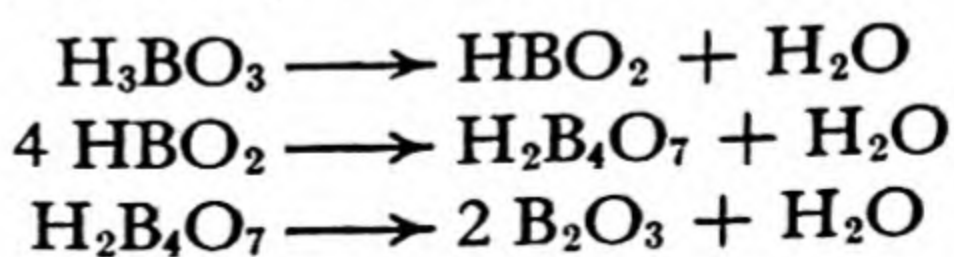
The reaction of boric acid with sodium hydroxide yields the tetraborate.

$$4\,H_3BO_3 + 2\,OH^- \rightleftharpoons B_4O_7^{--} + 7\,H_2O$$
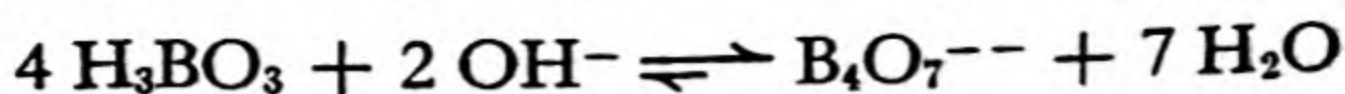
Boric acid reacts with methanol in the presence of sulfuric acid to form methyl borate, $(CH_3)_3BO_3$. This compound is volatile and burns with a green flame. This property may be applied as a test for borates.

Borax. At temperatures below $60°$, this salt crystallizes from solution as the decahydrate, $Na_2B_4O_7(H_2O)_{10}$. Borax hydrolyzes to give basic solutions.

$$B_4O_7^{--} + 7 H_2O \rightleftharpoons 4 H_3BO_3 + 2 OH^-$$
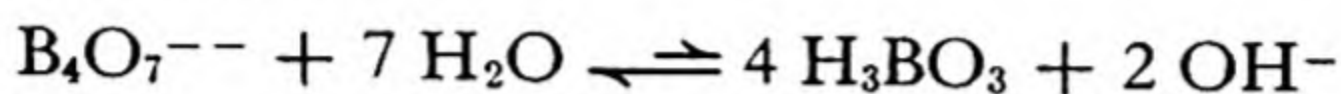
Because of this property, borax is used in households as a cleansing agent and to neutralize acidic impurities, such as calcium bicarbonate, in surface waters.

Fused borax reacts with basic substances in a reaction similar to the salts of other condensed acids. A mixture of metaborates is formed by the reaction of fused borax with metal oxides.

$$Na_2B_4O_7 + CoO \longrightarrow 2 NaBO_2 + Co(BO_2)_2$$
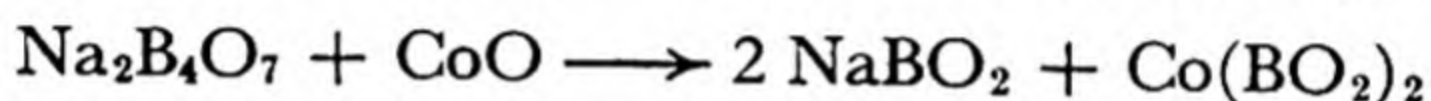
Tests for some of the metal ions may be based on the color of the metaborate produced in this reaction. Some of the characteristic borax bead colors are listed in Table 33.

TABLE 33. BORAX BEAD COLORS

Element	Reducing Flame	Oxidizing Flame
Cobalt	Blue	Blue
Chromium	Green	Green
Copper	Red	Blue
Iron	Green	Yellow
Manganese	Colorless	Violet

The use of borax as a flux in soldering and welding depends on the acidic properties of the fused material. Enamels are made by melting borax with glass, forming a glasslike product of low melting point. The addition of calcium phosphate, stannic oxide, or calcium fluoride produces a white enamel.

Sodium Peroxyborate. This compound, commonly called sodium perborate, may be prepared by the reaction of hydrogen peroxide with borax in basic solution.

$$B_4O_7^{--} + 2 OH^- + 4 H_2O_2 \rightleftharpoons 4 BO_3^- + 5 H_2O$$
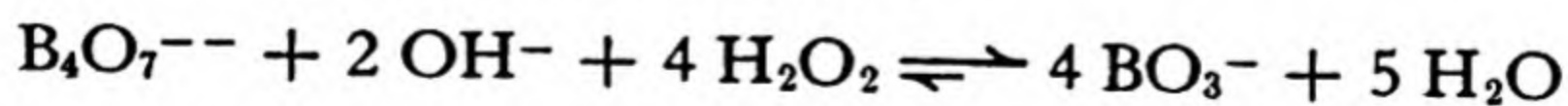
This ion contains the peroxy group of atoms. (See page 310.) The salt hydrolyzes to form hydrogen peroxide. Consequently, the so-

lution has bleaching action. It is used as an antiseptic material in certain tooth powders.

EXERCISES

1. Describe the allotropes of carbon, and discuss their economic importance.
2. Write equations for the reaction of carbon with each of the following: (a) steam; (b) zinc oxide; (c) bismuth oxide; (d) arsenic trioxide; (e) potassium bromate; (f) calcium phosphate; (g) calcium phosphate and silicon; (h) calcium oxide; (i) sulfur; (j) silicon dioxide and chlorine.
3. Describe the production of carbon dioxide both in laboratory practice and in industrial processes.
4. What equilibria exist in a solution of carbon dioxide? Discuss the effect on these equilibria of (a) heating the solution, (b) cooling the solution, (c) increasing the pressure of carbon dioxide, (d) adding a base, and (e) adding an acid.
5. How may an insoluble carbonate be converted into a soluble bicarbonate? Explain.
6. What two methods may be used for the conversion of a bicarbonate into a normal carbonate? Explain.
7. How is carbon monoxide produced industrially? Discuss its importance.
8. What is producer gas? water gas? How are these fuel gases produced?
9. Describe the processes for the industrial production of (a) graphite, (b) calcium carbide, (c) silicon carbide, (d) carbon disulfide, (e) carbon tetrachloride.
10. Explain the basicity of solution of sodium carbonate, of sodium silicate, and of borax.
11. Explain the fact that the complex silicates react with sodium carbonate when the solid substances are heated together.
12. Discuss the production of glass, showing how the properties are altered through changes in the composition of the charge used in glass making.

SUPPLEMENTARY READINGS

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 9–11.

Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940, chaps. XIII–XIV.

Pierce, W. M., "Silicosis: Occurrence and Control," *Chem. Met. Eng.* **49,** 11, 110 (1942).

Killeffer, D. H., "The Industry of Solid Carbon Dioxide," *J. Chem. Education* **19,** 482 (1942).

Bogue, R. H., "Portland Cement and the Plastic Concrete," *J. Chem. Education* **19,** 36 (1942).

Cooper, H. C., "Modern Abrasives," *J. Chem. Education* **19,** 122 (1942).

Ridgway, R. R., "Manufactured Abrasives," *Chem. Eng. News* **21,** 858 (1943).

Flint, F. C., "Glass," *J. Chem. Education* **19,** 287 (1942).

"Plate Glass Manufacture," Pictured Flow Sheet, *Chem. Met. Eng.* **49,** 1, 114 (1942).

Chapter 24

THE COLLOIDAL STATE OF DISPERSION

A dissolved substance is in the molecular or ionic state and a solution is homogeneous. Solute particles diffuse readily into a layer of the pure solvent in contact with the solution. Finely divided solids produce suspensions when they are stirred or shaken with a liquid in which they are not soluble. The suspension is a heterogeneous mixture. In a coarse suspension the particles of the solid are visible to the unaided eye. They usually settle when the suspension is allowed to stand, and may be separated from the liquid by filtration. There is an intermediate range between the solution and the mechanical mixture, in which the dispersed material retains its former phase, but the particles are so small that they are not visible to the eye and do not separate on standing. Such systems are called *dispersed systems*. The particles in such systems do not diffuse readily into a supernatant layer of the dispersing liquid. The name *colloid*, from the Greek word meaning glue, was used by Graham for the substances that readily form dispersions of this type. Substances yielding solutions more readily were called *crystalloids*. It was soon recognized, however, that many crystalline substances also produce dispersions that are not solutions. The name colloid is now applied to dispersed systems containing two or more substances, rather than to the substance dispersed. The colloidal state of dispersion is intermediate between solution and mechanical suspension.

Size of the Particles in the Colloidal State. A colloidal system is a heterogeneous system in which the dispersed material is distributed uniformly in a fine state of subdivision throughout the dispersing medium. Ostwald first classified such systems on the basis of the size of the particles in the dispersed phase. The smallest particles in the ordinary coarse suspensions are about 5×10^{-5} cm. along any dimension. These particles do not pass through a filter

paper and do not diffuse. They are visible with the aid of the microscope. Particles having dimensions less than 1×10^{-7} cm. diffuse rapidly, pass through filter paper, and exhibit all of the properties of solute particles. *Colloidal dispersions* are systems in which the dispersed phase consists of particles having at least one dimension ranging between 5×10^{-5} cm. and 1×10^{-7} cm. These limits are between microscopic visibility and particles rather larger than ordinary molecules. There is no sharp line of distinction between colloidal dispersions and slow-settling suspensions at one extreme, nor between colloidal dispersions and true solutions at the other. The limits assigned to the colloidal state are arbitrary. There are substances, such as egg albumen, that may be dispersed into molecular particles which, nevertheless, fall in the colloidal range because they are composed of such large molecules.

Types of Colloidal Systems. These systems may be classified according to the state of the matter involved. Consequently, there are eight general classes of colloids, *viz.*, solids, liquids, and gases in liquids; solids, liquids, and gases in solids; and solids and liquids in gases. The more familiar systems are those in which the dispersing medium is either liquid or gaseous. Systems containing solids dispersed colloidally in liquids are commonly called *colloidal solutions*. The colloidal dispersions of solids in water are often called *hydrosols*. Dispersions of liquids in liquids are *emulsions*. Dispersions of gases in liquids, as lather from a soap solution, are foams. Solids and liquids dispersed in gases are *aerosols*. Smoke and fine dust particles are solid aerosols. Some systems have a network structure of the interlacing type, in which the solid and liquid phases are continuous throughout the entire sample. These systems are *gels*.

Liquid systems in which the attraction between the dispersing medium and the dispersed phase is great are called *lyophilic colloids*, in aqueous medium, *hydrophilic*, *i.e.*, "water loving." Such systems are easily obtained because the separate materials may be brought into colloidal state by shaking or stirring. Hydrophilic systems are called reversible colloids. Systems in which the attraction between the two materials is small are *lyophobic colloids*, in water, *hydrophobic*, *i.e.*, "water fearing." The dispersed material in this type of colloid is readily coagulated, causing it to separate from the dispersing liquid. Usually, such materials are not redispersed by the ad-

dition of the liquid. Hydrophobic systems are called irreversible colloids.

Properties of Colloidal Dispersions. Colloidally dispersed particles in liquid systems pass through filter paper and do not separate from the liquid when standing. Certain materials, such as parchment paper, animal membranes, and cellophane, serve as a porous diaphragm that permits the diffusion of dissolved materials but does not permit the passage of particles of colloidal size. This property may be applied to secure a separation of soluble substances from colloidally dispersed materials by a process known as *dialysis*. The colloidal suspension containing the dissolved materials is placed in a dialyzing cup, which may be made in a simple form by binding cellophane over the open end of a glass cylinder. The cup is now suspended in a vessel through which fresh water flows. Dissolved substances pass out through the cellophane diaphragm and are washed away, while the colloidal material is retained in suspension in the dialyzing cup.

The most noticeable differences in properties between colloidal dispersions and coarser suspensions are due to the fine state of subdivision of the colloidal particles. The more finely divided the substances are, the greater the number of particles and the total area of the surface exposed for the same weight of material. The total surface of a cube with 1 cm. edges is 6 sq. cm. If this cube were cut in half along each of its three dimensions, there would be eight cubes, with $\frac{1}{2}$ cm. edges, and the total surface would be 12 sq. cm. If this process of subdivision were continued to the lower limits of colloidal size, the total surface area would be approximately $1\frac{1}{2}$ acres. In the surface boundary between two phases of matter, atoms, ions, and molecules are in different relation to adjacent particles than in the interior of a solid. The discontinuity causes specific properties which are dependent on forces existing at the surface, and such properties become more prominent as the size of the particles is made smaller. *The dispersed particles in colloidal systems are so small that surface forces play an important role in determining the properties of the substance.*

The Tyndall Effect. The path of a beam of light through a colloidal suspension is visible as a turbid area, while no visible path can be observed through a solution. This phenomenon,

called the Tyndall effect, shows that the dispersed particles in the colloidal material are large enough to present reflecting sur-
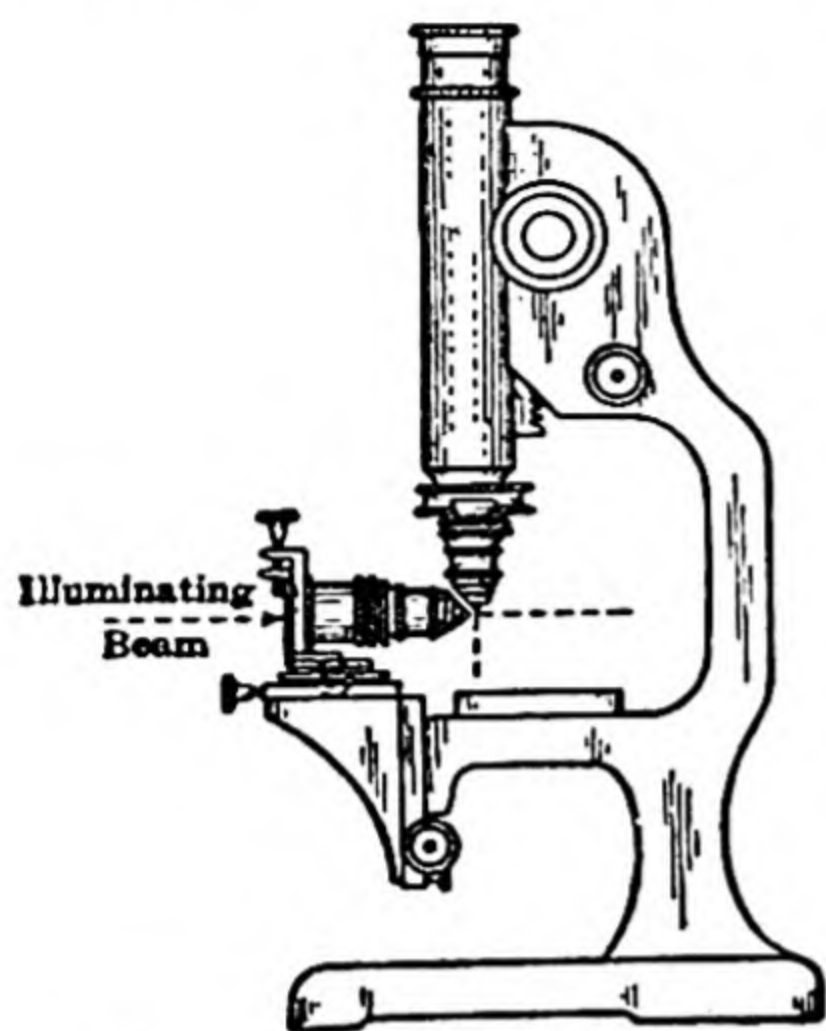
Fig. 107. Ultramicroscope

faces to light. This effect is not observed in solutions, because the molecules and ions into which solutes are dispersed are too small. The position of the individual particles in an illuminated area may be detected by the use of the *ultramicroscope*. A powerful transverse beam of light is brought to a focus within the suspension, and this area is examined by a microscope at right angles to the path of the beam. (Fig. 107.) Minute bright specks can be seen against a dark background, but no such effect can be observed in solutions.

Brownian Movement. Particles of colloidal magnitude are in rapid erratic motion in the dispersing medium. The apparent position of a single particle at successive equal intervals of time, as viewed through the ultramicroscope, may be projected on a plane. Lines connecting these points show a zigzag path between the points *A* and *B*. (Fig. 108.) The actual path of the particles is, of course, much more erratic and complex. This phenomenon, first observed by Brown, a Scottish botanist, is called the Brownian movement. Molecules of the dispersing medium are in rapid motion, and they continually strike against the colloidally dispersed particles. At a particular instant,

Fig. 108. Brownian Movement

a single particle moves in the direction of the resultant of all of the forces of impact. The mean free path of the particle is small, and the observed motion is along a haphazard path, because the molecules of the liquid or gaseous dispersing medium are moving at random. The Brownian movement tends to cause colloidal particles to remain dispersed.

Electric Charges of the Particles in Colloidal Suspension.
Colloidally dispersed particles almost always carry an electric charge. This may be shown by placing a colloidal suspension beneath water in a large U-tube, and inserting electrodes connected with a source of direct current into the clear liquid. When colloidal arsenious sulfide is tested in this manner, it is found that the colloidal particles move toward the anode, showing that they bear negative charges. (Fig. 109.) Commonly, many of the metal sulfides and the free noble metals form negatively charged particles in the colloidal state. The source of this charge cannot be stated with certainty in all suspensions, although it is probably due to the adsorption of specific electrically charged ions from the solution. The charges of the collodial particles are balanced by the charges of free ions in the solution. Because of their electric charges, the dispersed particles repel each other, and their coalescence to form larger and heavier particles is prevented.
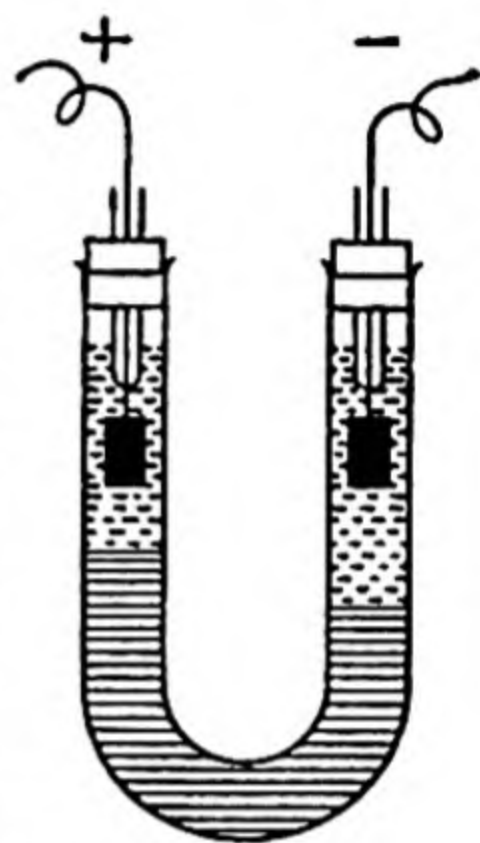
Fig. 109

Preparation of Colloidal Dispersions. The methods for the preparation of colloidal materials fall into two classes, dispersion methods and condensation methods. *Dispersion methods* are those in which coarser aggregates of matter are subdivided into particles of colloidal size. The disintegrating action of the dispersing medium reduces many materials to the colloidal state, just as the solvent action of a liquid causes a soluble substance to dissolve. This process is called *peptization.* Water is absorbed by substances such as tannin, gelatin, and agar to form colloidal materials. Such systems are lyophilic colloids. Some solids are peptized by ions adsorbed from solution; *e.g.*, metal sulfides may be peptized by sulfide and hydrosulfide ions, with the formation of negatively charged particles repelling one another. This may be sufficient to cause a precipitate to become colloidally dispersed. In other instances the stability of a precipitate may be due to the presence of an adsorbed salt. Such substances are called *agglomerating agents.* In such instances, a colloidal dispersion sometimes results when the salt is washed out of the precipitate. Peptization by ions and by the removal of the agglomerating agent is frequently encountered in analytical

chemistry, and often causes trouble in handling precipitated sulfides and hydrated metal oxides.

Many solids may be broken down into particles of colloidal magnitude by *grinding*. The finely ground powder produces a colloidal suspension when it is agitated with a liquid, unless particles coalesce during the latter stage of the process. Colloidal silica may be produced by suspending finely ground quartz in hot water. "Colloid mills" have been devised for grinding solids to produce colloidal suspensions. The pigment zinc oxide consists of aggregates of very fine particles that must be suspended uniformly throughout the oil in the preparation of paint. This may be accomplished by grinding the oxide with the vehicle in a colloid mill.

In *condensation methods* particles of colloidal size are produced by the union of smaller particles such as molecules, atoms, and ions. The methods employed lead to the formation of insoluble products, but by establishing special conditions a colloidal suspension is produced instead of a precipitate. The absence of ionic materials that would cause precipitation of the insoluble product must be insured, and requisite concentrations must be supplied of the specific ions that keep the particles in colloidal state. Many metals may be produced in colloidal state by *the Bredig arc method*. In this method a current of 5–10 amperes at 110 volts is passed between wires of the metal so as to form an arc beneath the surface of cold water. (Fig. 110.) The metals vaporize, and the vapor condenses immediately, producing the colloidal metal. A low concentration of hydroxide ions helps to stabilize the metal colloid absorbing these ions.
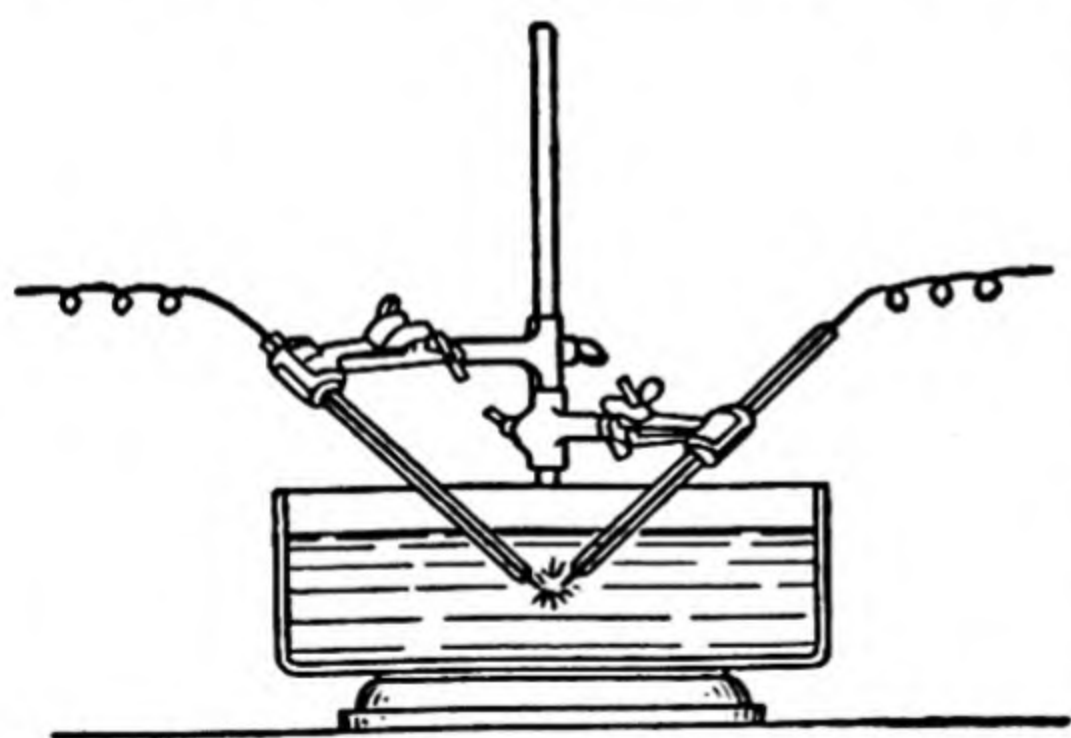
Fig. 110. Bredig Method

Colloidal suspensions of some of the metals result from *oxidation-reduction reactions* in solution. Colloidal sulfur is commonly formed when metal sulfides are oxidized by nitric acid in analytical procedures. Colloidal gold may be prepared by the reduction of gold chloride in dilute solution by phosphorous acid, tannin, or hydro-

quinone. Colloidal gold exhibits different colors, red, blue, or purple, depending on the size of the particles. Faintly ammoniacal solutions of silver salts yield a dark brown colloidal suspension when they are reduced by tannin and certain other reducing agents.

Reactions producing insoluble compounds frequently yield colloidal dispersions. The passage of hydrogen sulfide into a solution of arsenious acid containing a strong acid yields a precipitate.

$$2\ H_3AsO_3 + 3\ H_2S \longrightarrow As_2S_3 \downarrow + 6\ H_2O$$

The reaction of hydrogen sulfide with dilute solutions of arsenious acid, containing no strong acid, produces a yellow colloidal dispersion. This colloid is sensitive to hydrogen ions.

The stability of silver halide colloids is increased by an excess of either the silver salt or the halide. In the former solution, the adsorption of silver ions produces positively charged colloidal particles, in the latter, the adsorption of halide ions produces negative particles.

Colloidal metal hydroxides may be prepared by the *hydrolysis of certain hydrated cations*, such as the ferric ion. A dark red colloidal dispersion may be produced by pouring a concentrated solution of ferric chloride slowly into hot water. The product, commonly called ferric hydroxide, is more accurately named hydrous ferric oxide, because the ratio of water to the oxide is not definite as required for the hydroxide. This product is acidic in nature and its stability is increased by the presence of the hydrogen ions produced during hydrolysis.

Precipitation of Colloidally Dispersed Solids. Colloidal solid particles remain in the dispersed phase primarily because the electric charges they bear prevent coalescence to form heavier particles. Consequently, it is necessary to alter the charges of the particles to cause precipitation. The charge of the colloidal particle is usually due to adsorbed ions. Hence, the precipitating ions must have the opposite charge, so that they may remove the adsorbed ions, or be themselves adsorbed, thus balancing the charge. In general, ions having high electric charges are more effective than those having lower charges. Many colloidal particles may react to release protons or to gain protons. Such particles are most easily

precipitated under ion concentrations that balance these two effects. Under such conditions the particle does not migrate in an electrical field. The concentration of hydrogen ions at which colloidally dispersed particles do not migrate in an electric field is known as the *isoelectric point*.

Colloidal particles of arsenious sulfide are negatively charged. This system is broken with the precipitation of arsenious sulfide by the addition of ions neutralizing this charge. The addition of acids causes the precipitation of arsenious sulfide from the dispersion. Particles of colloidal ferric hydroxide are positively charged. The precipitation of this substance is brought about by the addition of negative ions such as hydroxide, carbonate, or phosphate. Oppositely charged colloidal particles mutually coagulate each other.

Many rivers carry large quantities of colloidally dispersed solids, in addition to materials in coarser suspensions. When such muddy river water enters the ocean and becomes mixed with sea water, the colloidal material is precipitated as a result of the coagulating effect of the dissolved salts.

Protective Colloids. Many colloidal suspensions are stabilized by the use of the proper proportion of some other colloidal substance. If dilute solutions containing equivalent quantities of silver nitrate and potassium bromide are mixed, a precipitate of silver bromide is formed at once. If, however, gelatin is added to each of the solutions before they are mixed, a clear colloidal dispersion of silver bromide is produced. Gelatin is itself a colloidally dispersed material, and it acts as a protective colloid in stabilizing the silver bromide suspension. The use of gelatin is of great importance in the preparation of light-sensitive silver salts in the proper state of subdivision for use in the manufacture of photographic films, plates, and printing papers. The protective colloid is in general hydrophilic in nature and its effect is due to the formation of a thin film of the protective colloid adsorbed on the surface of the dispersed solid.

Gels. Precipitates which contain relatively large proportions of the liquid in which they are formed are known as *gelatinous precipitates*. If the insoluble substance coagulates to retain all of the liquid, the product is a *jelly*. The setting of jellies may be attributed to the formation of minute fibers and films of the dispersed material in a

cellular structure that retains the liquid by capillary attraction and by combination with the fibers. Often when jellies are allowed to stand, some of the free liquid separates with a corresponding decrease in the volume of the jelly. This phenomenon is known as *syneresis*. It is attributed to the gradual growth of the minute particles of the dispersed material into larger aggregates with a decrease in the surface area for the same weight of material. On account of this change, some of the dispersing liquid is set free.

Fruit juices containing enough pectin, as the juices of apples, currants, and grapes, yield jellies when sugar is added and the solutions are concentrated to the proper degree. In making "solidified alcohol," employed for special purposes as a fuel, cellulose esters are used to cause the formation of jelly. When hydrochloric acid is added to a solution of a soluble silicate, insoluble hydrated silica is formed. Under certain conditions this reaction yields a clear colloidal suspension which soon sets to form silicic acid jelly. The dehydration of this jelly produces a very porous solid, known as *silica gel*, which has extensive commercial applications as an adsorbent. Nitroglycerine may be gelatinized by nitrocellulose to form blasting gelatin.

Emulsions. Emulsions are usually prepared by shaking or stirring immiscible liquids together. Emulsions prepared in this way usually separate into layers of the original components, unless an *emulsifying agent* is present. In order to produce lasting emulsions, one of the liquids is dispersed into fine droplets which become coated with a protecting film of the emulsifying agent. In this way the coalescence of the droplets is prevented. Different emulsifying agents are required for different liquids. The kerosene and water emulsions used in spraying fruit trees may be prepared through the use of soap as the emulsifying agent. Eggs supply the emulsifying agent in the production of mayonnaise from olive oil and vinegar. Milk and cream are emulsions of butter fat in water, with casein as the emulsifying agent. The fat droplets vary in size from 2×10^{-4} cm. to 1×10^{-3} cm. in diameter. In the process of homogenizing milk, the droplets are reduced to a small fraction of these sizes, so that the total surface area of the droplets is greatly increased, thus increasing the stabilizing effect of the emulsifying agent.

The breaking of an emulsion is caused by the destruction of the

protecting film. Substances that react with the emulsifying agent may cause this effect. The addition of hydrochloric acid to the kerosene-water emulsion in which soap is the emulsifying agent causes the emulsion to break by reacting with the soap to form a weak acid. The emulsifying film may be broken in a number of ways, e.g., by the addition of an excess of the dispersed phase, by the addition of an excess of common salt that causes "salting out" by dehydrating the film, by the application of high electrical potential, by centrifugal action, and in some instances, by heating or by freezing the materials. The breaking of emulsions is often of great industrial importance.

Foams. A foam is a dispersion of a gas in a liquid. Gas bubbles, like liquid droplets in emulsions, are enclosed in films. Gas bubbles are generally much larger than the droplets in emulsions, but the thickness of the enclosing films brings them into the colloidal state. Foams are usually formed by shaking liquids in air. Stable foams result if the liquid is viscous enough to form long-lived films, or if the film is stabilized by the presence of finely divided solids at the boundary between the liquid and gas. Many hydrophilic colloidal materials, such as saponin and protein, produce stable foams.

Dust. Smoke. Fog. Dusts contain finely divided solid particles in air; smokes usually contain both solids and liquids; and fogs, mists, and clouds consist primarily of liquid droplets. Usually, liquid dispersions in air are formed by the condensation of gaseous materials around a nucleus of dust particles, so that no sharp distinction can be drawn between liquid and solid aerosols in such natural materials.

Smoke and fog result from the condensation of gaseous materials and from the interaction of gaseous substances. Solid particles too may be carried along mechanically. Great clouds of smoke, dust, and fog are observed in industrialized areas. Most of the materials carried along in smokes, dusts, and fumes are objectionable, some are dangerous, and some are valuable. Hence, the separation of these materials from air is important. *The Cottrell process* for the elimination of smokes, and the recovery of such valuable materials as they may contain, involves the passage of flue gases between plates bearing high electric charges. The dispersed particles, being themselves electrically charged, are attracted to the plates and

deposited, allowing uncharged gas molecules to pass on into the air.

Adsorption. Since adsorption is dependent on surface forces, the extent of adsorption is greatest when the adsorbent is finely divided or porous. The amount of the substance adsorbed, however, is not dependent merely on the state of subdivision of the adsorbent, but depends also on the properties of both the adsorbent and the adsorbed substance. *Adsorption is a selective process.* Gases having high critical temperatures are usually adsorbed to a greater degree than those having low critical temperatures. The quantity of a gas adsorbed by a given weight of an adsorbent is increased by increasing the pressure.

A very porous form of charcoal may be prepared from coconut shells and the pits of some fruits. This material is particularly efficient for the adsorption of gases and fumes. It is extensively used in the canisters of gas masks for protection from chemical warfare agents such as mustard gas and lewisite, and from poisonous gases liberated in certain industrial accidents. As air is drawn through charcoal in the canister these substances are adsorbed to such an extent that the proportions remaining in the air are not dangerous, while oxygen and nitrogen are not appreciably adsorbed at ordinary temperatures. Such gas masks are not effective for gases of low critical temperature.

The use of aluminum sulfate and of iron salts in the clarification of water in filtration plants depends on two effects. The highly charged positive ions of these salts aid in coagulating the negatively charged colloidally dispersed particles in the water. These ions also interact with water and basic solutions forming positively charged particles of a gelatinous nature. Such particles adsorb suspended matter and are themselves coagulated to form easily filterable precipitates. The coagulation of colloidal materials in sewage disposal plants is an important process.

Most dyes go into colloidal suspension in the dye solution. Many dyes are adsorbed directly by animal and vegetable fibers, but there are few direct dyes for cotton cloth. In order to dye such materials a mordant is used. The *mordant* is a salt of some high-valent metal ion, such as aluminum or tin, which forms a gelatinous, colloidal hydrous oxide throughout the fiber. Such

materials are adsorbed by the fiber and they, in turn, adsorb the dye. The mordant may be stamped in a pattern in the cloth which is then soaked in the dye. When the dyed cloth is subse-quently washed, the dye is washed out, except in the mordanted portions, leaving the desired printed goods.

EXERCISES

1. What are colloidal dispersions? How do they differ from ordinary coarse suspensions and from solutions?
2. What is meant by dialysis? How is it related to filtration?
3. What are the various classes of colloidal systems?
4. What is the Tyndall effect? To what is it due?
5. What is the Brownian movement?
6. What is the effect of electric charges on the stability of colloidal systems?
7. What two classes of methods may be used for the preparation of colloidal dispersions? Give examples to illustrate each class.
8. How can the particles in colloidal suspensions be coagulated? Give examples to show the importance of coagulating such materials.
9. How are emulsions prepared? How can they be caused to break?
10. What is a protective colloid? Explain its action in stabilizing colloidal dispersions.
11. How do gels and jellies differ in structure from the other types of colloidal systems discussed?
12. What is meant by adsorption? Discuss some of the important applications of adsorption in industrial processes and in analytical separations.

SUPPLEMENTARY READINGS

Weiser, H. B., *Colloid Chemistry*, John Wiley & Sons, Inc., New York, 1939.

Hildebrand, J. H., *Principles of Chemistry*, The Macmillan Company, New York, 1940, chap. XIX.

Alexander, J. A., *Colloid Chemistry, Theoretical and Applied*, Chemical Catalog Company, Inc., New York, 1932.

Graham, T., *Phil. Trans. Roy. Soc.*, London **151**, 183 (1861).

Nicholson, D. G., "Chemical Agents as Screening Smokes," *J. Chem. Education* **20**, 499 (1943).

Chapter 25

SALTS OF SODIUM, POTASSIUM, AND AMMONIUM

The alkali metals are the elements of Group I of the periodic system, *viz.*, *lithium*, *sodium*, *potassium*, *rubidium*, and *cesium*. The free elements are prepared by the usual methods for the production of metals of high activity, the electrolysis of a fused compound. The metals and their hydroxides are discussed in Chapter 10, page 146. The alkali metals are active metals which readily give up an electron per atom to form ions having an oxidation number of 1 +. These ions are relatively stable toward reduction. The hydroxides of the alkali metals are strong bases, and the ions of the metals do not undergo hydrolysis. There are a large number of salts, containing ions of the alkali metals. The salts are ionic in structure, and most of them are soluble in water. Consequently, they are common laboratory reagents to provide the different anions. The salts of sodium and potassium are the most important of the salts of the alkali metals. Ammonium salts are similar in many respects to the salts of sodium and potassium.

Reactions of Sodium, Potassium, and Ammonium Ions. There are few precipitation reactions of these cations, because all of their common salts are soluble. Sodium pyroantimonate may be obtained as a white precipitate by the reaction of solutions of potassium pyroantimonate with sodium salts.

$$Na^+ + Sb(OH)_6^- \rightleftharpoons NaSb(OH)_6 \downarrow$$
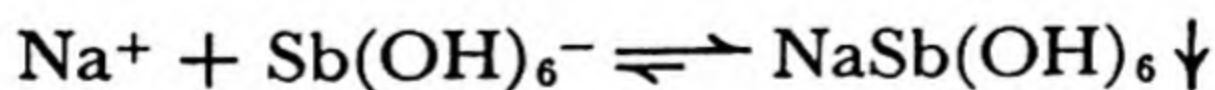
The hydrogen tartrate salts of potassium ions and of ammonium ions are precipitated as white crystalline salts from neutral solutions, and both of these ions yield yellow precipitates by reaction with sodium cobaltinitrite and with chloroplatinic acid.

411

$$K^+ + HC_4H_4O_6^- \rightleftharpoons KHC_4H_4O_6 \downarrow$$
$$2\,NH_4^+ + Na^+ + Co(NO_2)_6^{---} \rightleftharpoons (NH_4)_2NaCo(NO_2)_6 \downarrow$$
$$2\,K^+ + PtCl_6^{--} \rightleftharpoons K_2PtCl_6 \downarrow$$
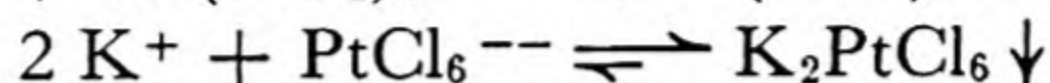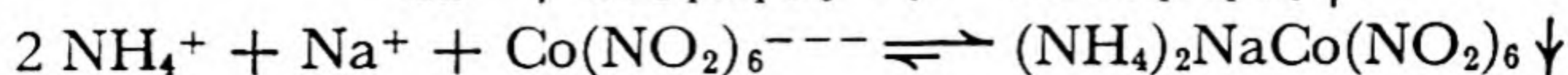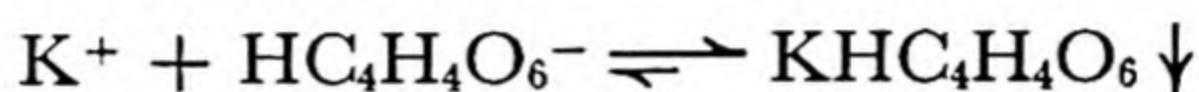
Usually, these salts precipitate readily from concentrated solutions, but only slowly from dilute solutions. Ammonium salts react with strong bases, forming ammonia and water.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$
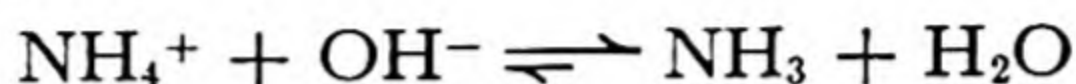
The Chlorides. The chlorides of sodium, potassium, and ammonium exhibit the general reactions characteristic of chloride ions. The solid salts react with acids of high boiling point to produce gaseous hydrogen chloride.

$$2\,NaCl + H_2SO_4 \longrightarrow 2\,HCl \uparrow + Na_2SO_4$$
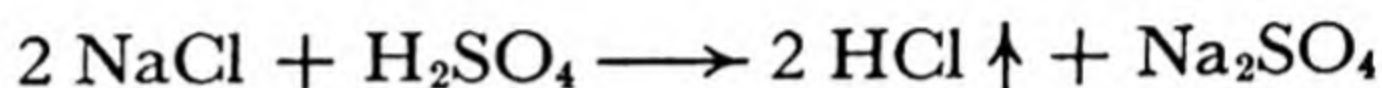
With strong oxidizing agents in the presence of hydrogen ions they yield free chlorine.

$$2\,Cl^- + MnO_2 + 4\,H^+ \longrightarrow Cl_2 + Mn^{++} + 2\,H_2O$$

Electrolysis of solutions of the alkali metal chlorides produces chlorine at the anode, hydrogen at the cathode, and a solution of the metal hydroxide in the cathode compartment of the cell. These salts react with solutions of silver, lead, and mercurous salts, precipitating the slightly soluble chloride.

$$Cl^- + Ag^+ \rightleftharpoons AgCl \downarrow$$
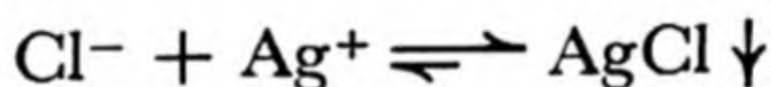
These reactions are properties of chloride ions.

Salt Beds. Approximately two thirds of the soluble material in sea water is sodium chloride. Great salt beds composed largely of this salt are found in different parts of the world. Beds of soluble salts have been formed by the evaporation of sea water and the water in salt lakes. Soluble salts, leached from the soil, gradually accumulate in such bodies of water as evaporation proceeds. The water usually becomes saturated with sodium chloride first, because of its greater abundance, and successively with other minerals during long-continued evaporation. Consequently, the composition of the salt mixtures varies in different strata. Usually, the bottom layer of the deposit is composed primarily of rock salt, sodium chloride. The upper strata contain the less abundant and more solu-

ble materials. In the Stassfurt deposit, there is a layer of rock salt approximately 2000–3000 ft. thick. Above this is a stratified deposit, 50–60 ft. thick, containing chlorides and sulfates of calcium, magnesium, sodium, and potassium. This layer consists chiefly of the complex crystalline salts: *polyhalite*, $(CaSO_4)_2MgSO_4K_2SO_4(H_2O)_2$, *carnallite*, $KClMgCl_2(H_2O)_6$, and *kieserite*, $MgSO_4H_2O$, with interspersed layers of *tachydrite*, $CaCl_2(MgCl_2)_2(H_2O)_{12}$, *boracite*, $(Mg_3B_8O_{15})_2MgCl_2$, *kainite*, $K_2SO_4MgSO_4MgCl_2(H_2O)_6$, *schoenite*, $K_2SO_4MgSO_4(H_2O)_6$, and *sylvine*, KCl. It is only in relatively thick deposits that the percentage of potassium chloride is great enough to serve as an important source of this salt.

Sodium Chloride. NaCl. This salt is obtained from salt mines, salt wells, and sea water. The impure salt thus obtained may be purified by recrystallization. This process consists in dissolving the salt and again evaporating the solution until a large proportion of the sodium chloride has separated. At higher temperatures, most of the impurities are much more soluble than sodium chloride, and therefore they remain in solution. Pure salt may be precipitated by passing hydrogen chloride gas into the saturated solution. In part this is due to the great increase in the concentration of chloride ions. Under these conditions, the dehydrating action of the hydrogen chloride gas is also a factor in causing the precipitation of sodium chloride.

Sodium chloride crystallizes in the regular cubic system. It melts at 801°, and the liquid is significantly volatile at temperatures around the melting point. The solubility of sodium chloride is 35.7 g. in 100 g. of water at 0°, and 39.12 g., at 100°. The pure salt does not deliquesce under ordinary conditions of humidity and temperature, but may do so in contact with the high pressures of water vapor in the air in hot humid weather. Even small proportions of magnesium chloride in salt cause it to become moist in humid weather and to cake. Salt is an essential ingredient of animal food, and has extensive industrial uses in the production of sodium compounds, such as the hydroxide, the carbonate, and other salts prepared from these two substances. It is also the principal source of chlorine, hydrochloric acid, and of all the products made from these two substances. In addition, there are a number of miscellaneous products made directly or indirectly from common salt.

Potassium Chloride. **KCl.** Potassium chloride is the source of most potassium salts, but its most extensive use is as a plant fertilizer. Before World War I, potassium chloride was secured primarily from the Stassfurt deposits and other deposits in Germany. The production of potassium salts from deposits in the United States is at the rate of 700,000 tons annually, calculated in terms of the potassium oxide equivalent. This is an adequate supply to fill industrial and agricultural requirements. The most important sources of potassium compounds in this country are in the Carlsbad region in New Mexico and the Searles Lake brines in California.

The Searles Lake deposit consists of an extensive bed of solid salts in a very complex mixture. The spaces between the crystals are filled with a saturated brine containing K^+, Na^+, Cl^-, CO_3^{--}, SO_4^{--}, $B_4O_7^{--}$, PO_4^{---} ions, and small percentages of other ions. The brine is pumped out and concentrated in evaporators until the solution is saturated with potassium chloride. During evaporation, large amounts of sodium chloride and the salt, $Na_2CO_3(Na_2SO_4)_2$, separate. When the solution has become saturated with potassium chloride, it is also nearly saturated with borax. If the solution cools slowly, a mixture of potassium chloride and borax separates, but the borax crystallizes very slowly, and it is possible to secure a crop of nearly pure potassium chloride crystals by cooling the solution quickly. After separating the potassium chloride, the mother liquor is kept in storage tanks for a few days, and the borax crystallizes from its supersaturated solution. The crude product is separated, dissolved in hot water, and recrystallized.

Ammonium Chloride. **NH₄Cl.** This salt, known also as *sal ammoniac*, is prepared by the reaction of ammonia with hydrochloric acid.

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$
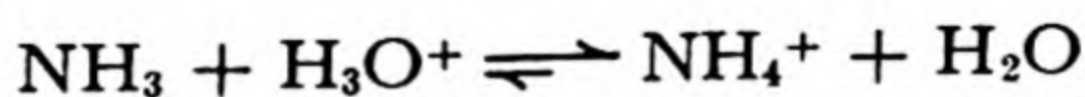
Ammonium chloride volatilizes when it is heated, giving a vapor pressure of one atmosphere in equilibrium with the solid at 338°. At this temperature, 62 per cent of the gaseous material is decomposed into ammonia and hydrogen chloride. Ammonium chloride is formed again as the gases cool, thus making possible the purification of this salt by sublimation. Ammonium chloride is used as a flux to remove metal oxides from the surface of metals during soldering, because it has acidic properties.

$$CuO + 2\,NH_4Cl \longrightarrow CuCl_2 + 2\,NH_3 \uparrow + H_2O$$
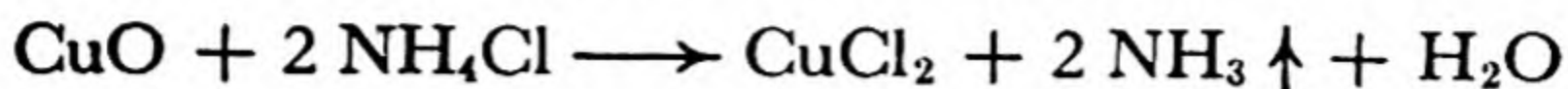
An extensive use of ammonium chloride is in the manufacture of dry cells. (See page 242.)

The Bromides. Small proportions of bromides are present in sea water and in salt well brines, but the direct crystallization of sodium bromide and potassium bromide from the brines is not practicable, because of the large proportions of other ions in the concentrated brines. Bromine is first prepared from the brines by displacement with chlorine.

$$2\,Br^- + Cl_2 \longrightarrow 2\,Cl^- + Br_2$$
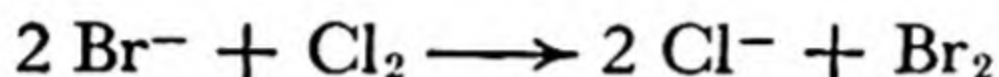
Bromides are then prepared by the reaction of bromine with hot solutions of the respective alkali metal hydroxides to form a mixture of the bromide and bromate.

$$3\,Br_2 + 6\,OH^- \longrightarrow BrO_3^- + 5\,Br^- + 3\,H_2O$$

The solutions are then evaporated to dryness and the bromate in the solid mixture is reduced to the bromide by heating with carbon.

$$KBrO_3 + 3\,C \longrightarrow KBr + 3\,CO$$

The bromide is extracted and is purified by recrystallization. These salts are used as sedatives and as laboratory reagents to supply bromide ions, but their most extensive industrial application is in the preparation of silver bromide for use in photography.

The Iodides. The iodides of sodium and potassium are prepared in the same manner as the bromides. Potassium iodide is the more common salt. Its principal use, like the bromide, is in the production of the silver salt. Iodized salt, common salt containing added iodides, is used in food in areas where the natural supply of iodides is inadequate. Thyroxine, an organic compound of iodine, is secreted in the thyroid gland. A deficiency of iodine interferes with the proper production of this compound and results in a type of goiter. Usually the necessary quantity of iodine is supplied in natural water and in mineral matter in vegetables.

The Cyanides. *Sodium cyanide* is usually prepared by fusing a mixture of calcium cyanamide and carbon with sodium carbonate.

$$CaNCN + C + Na_2CO_3 \longrightarrow CaCO_3 + 2\,NaCN$$
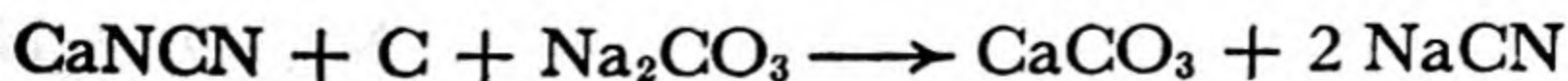
Sodium cyanide is extracted from the product by leaching with water. The cyanides are highly poisonous, and they react with acids producing gaseous hydrocyanic acid which is also very poisonous.

$$CN^- + H^+ \rightleftharpoons HCN$$
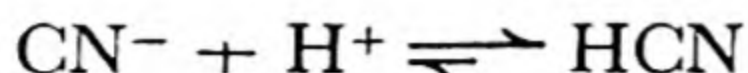
Aqueous solutions of the cyanides of sodium and potassium are strongly basic because of the hydrolysis of the cyanide ion.

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$
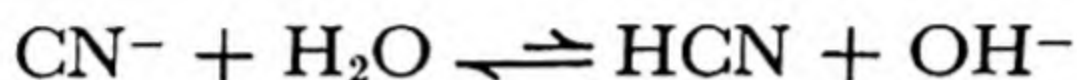
The soluble cyanides react with many of the metal ions with the formation of complex ions, e.g., complex cyanide ions of zinc, copper, iron, gold, and silver. An excess of the cyanide ions is required for this reaction.

$$Zn^{++} + 4\,CN^- \rightleftharpoons Zn(CN)_4^{--}$$
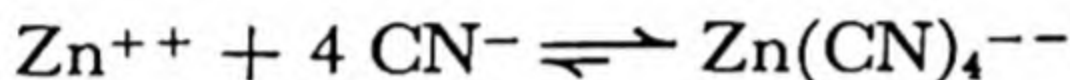
The fusion of an alkali metal cyanide with sulfur produces the complex thiocyanate.

$$KCN + S \longrightarrow KCNS$$
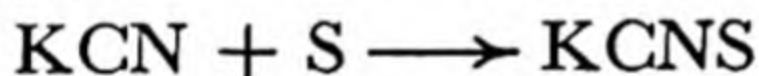
Sodium cyanide is used extensively in the extraction of gold and silver from ores and in the preparation of electroplating baths.

The Nitrates. When heated to temperatures well above their melting points the alkali metal nitrates decompose to form the nitrite and oxygen.

$$2\,KNO_3 \longrightarrow 2\,KNO_2 + O_2$$
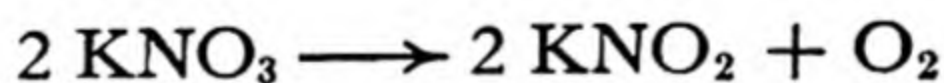
Ammonium nitrate decomposes into nitrous oxide and water when heated gently.

$$NH_4NO_3 \longrightarrow N_2O + 2\,H_2O$$
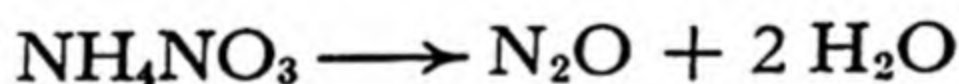
The nitrates of sodium and potassium are suitable oxidizing agents for use in the dry state and in fusion reactions that require the presence of basic substances such as, for example, the alkali metal hydroxides or carbonates. The fusion of sulfur with sodium nitrate and sodium hydroxide produces sodium nitrite and sodium sulfate. The equation representing oxidation-reduction in fusion reactions is easily balanced in terms of the changes in oxidation numbers. A convenient scheme for the determination of the correct coefficients involves first writing a skeleton equation:

$$NaNO_3 + S + NaOH \longrightarrow NaNO_2 + Na_2SO_4 + H_2O$$
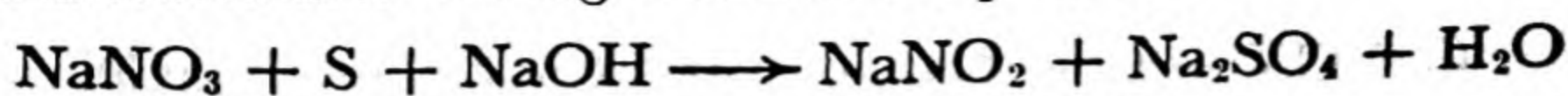
Next, the symbols and oxidation numbers of the element undergoing reduction may be written above the formula of the oxidizing agent and its reduction product, and a number may be written above the reaction symbol to show the change in oxidation number.

$$\overset{N^{5+}}{NaNO_3} + S + NaOH \xrightarrow{(-2)} \overset{N^{3+}}{NaNO_2} + Na_2SO_4 + H_2O$$
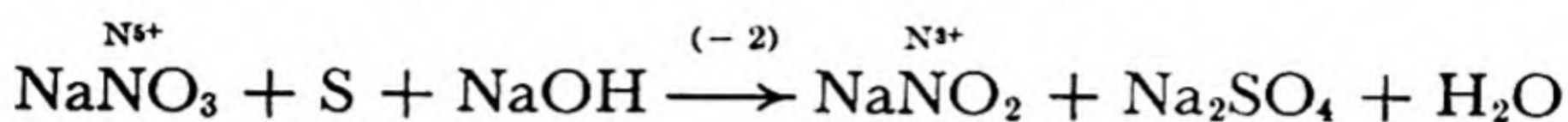
The change in oxidation numbers for the reducing agent may be shown in a similar manner by symbols and numbers beneath the respective formulas.

$$\overset{N^{5+}}{NaNO_3} + \underset{S^0}{S} + NaOH \xrightarrow[(+6)]{(-2)} \overset{N^{3+}}{NaNO_2} + \underset{S^{6+}}{Na_2SO_4} + H_2O$$
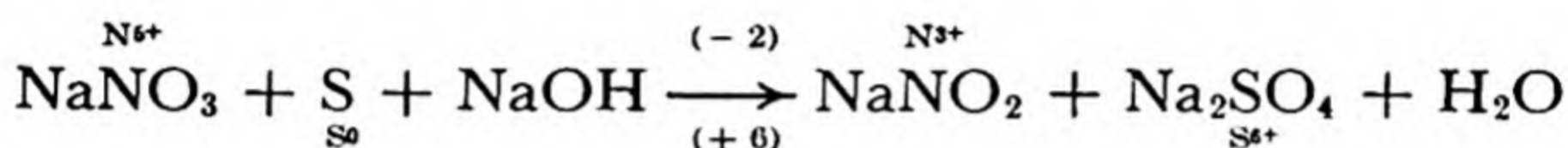
The molar ratio of the oxidizing agent and the reducing agent is obtained from the least common multiple of the oxidation number changes written above and below the reaction symbol. In this instance, the ratio is three of sodium nitrate to one of elementary sulfur. The balancing of the equation is then completed by inspection.

$$3\,\overset{N^{5+}}{NaNO_3} + \underset{S^0}{S} + 2\,NaOH \xrightarrow[(+6)]{3\times(-2)} 3\,\overset{N^{3+}}{NaNO_2} + \underset{S^{6+}}{Na_2SO_4} + H_2O$$
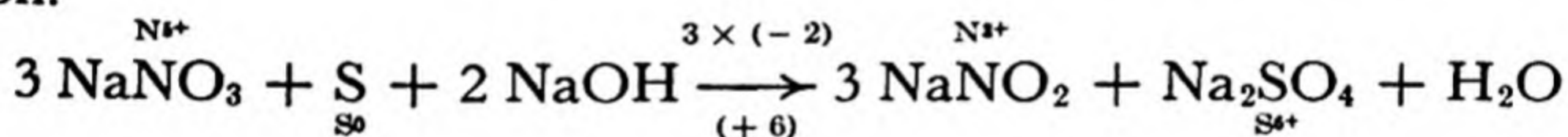
Sodium Nitrate. Chile Saltpeter. $NaNO_3$. Sodium nitrate occurs extensively in an arid region in Chile. The deposits are not uniform in composition, containing sodium nitrate in percentages varying from an unimportant proportion to 40–50 per cent. The material containing 20–50 per cent of sodium nitrate is leached with hot water to extract the soluble sodium nitrate. As the hot solution cools, sodium nitrate crystallizes, and the solid is separated from the solution. This cold saturated solution is reheated and used again in the extraction of fresh crude material. The solid obtained by this extraction process contains 95–98 per cent of sodium nitrate and is suitable for most industrial uses. Sodium nitrate is also prepared commercially by the reaction of synthetic nitric acid produced from atmospheric nitrogen with sodium hydroxide or sodium carbonate. Sodium nitrate is used in the production of sodium nitrite, potassium nitrate, nitric acid, and many other substances. Large quantities of this salt are used directly in plant fertilizers to supply available nitrogen.

Potassium Nitrate. Saltpeter. **KNO₃**. This salt is prepared from sodium nitrate and potassium chloride. The solubilities of potassium chloride, sodium nitrate, and potassium nitrate increase greatly with rise in temperature, but the solubility of sodium chloride increases only to a slight degree. Mixing hot saturated solutions of sodium nitrate and potassium chloride causes the precipitation of sodium chloride. The hot solution from which the precipitated sodium chloride has been removed now contains high concentrations of potassium and nitrate ions, but only low concentrations of sodium and chloride ions. Potassium nitrate crystallizes as the solution cools, but only a small proportion of sodium chloride separates along with it.

Potassium nitrate is an active oxidizing agent at elevated temperatures. Formerly, the chief use of this substance was in the manufacture of black gunpowder, a mixture containing approximately 75 per cent potassium nitrate, 15 per cent sulfur, and 10 per cent carbon. These substances react rapidly when the mixture is ignited, forming relatively large volumes of gaseous products consisting principally of nitrogen and oxides of carbon. This powder is suitable for use as a propelling explosive. The use of potassium nitrate in preference to sodium nitrate is due to its lower solubility at ordinary temperatures, which means that it does not take up moisture so readily. This type of gunpowder is no longer important, and now the nitrocellulose powders are used as propellent explosives. Potassium nitrate is used in some high grade fertilizers to supply both potassium and nitrogen in available form.

Ammonium Nitrate. **NH₄NO₃**. This white crystalline salt is prepared by the reaction of ammonia with nitric acid. When it is heated gently to a temperature somewhat above its melting point, 169.6°, ammonium nitrate decomposes to form nitrous oxide and water, but it yields nitrogen, oxygen, and water in a highly exothermic reaction when detonated.

$$2\,NH_4NO_3 \longrightarrow 2\,N_2 + O_2 + 4\,H_2O + 56{,}000\,cal.$$
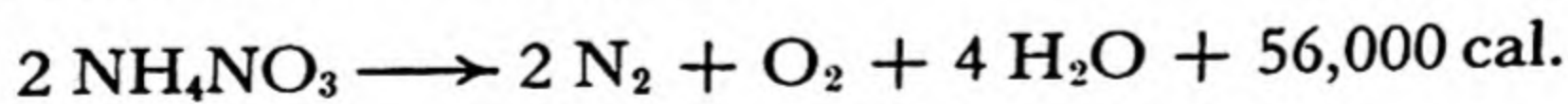
The salt is a high explosive but it is not easily detonated. A mixture of ammonium nitrate and trinitrotoluene is used in shells as a military explosive called *amatol*. Ammonium nitrate is also used in dynamite.

The Sulfides and Polysulfides. The sulfides of sodium, potassium, and ammonium are soluble in water. They are usually prepared for laboratory use by the reaction of hydrogen sulfide with the appropriate basic hydroxide. The hydrosulfide is formed when the basic solution is saturated with hydrogen sulfide.

$$H_2S + OH^- \rightleftharpoons HS^- + H_2O$$
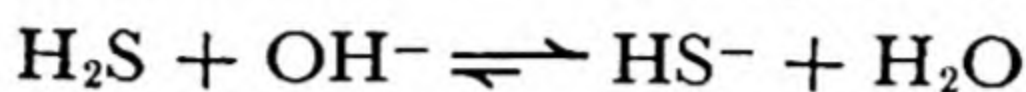
The normal sulfide may be prepared from the hydrosulfide by the addition of an equimolar quantity of the basic hydroxide.

$$HS^- + OH^- \rightleftharpoons S^{--} + H_2O$$
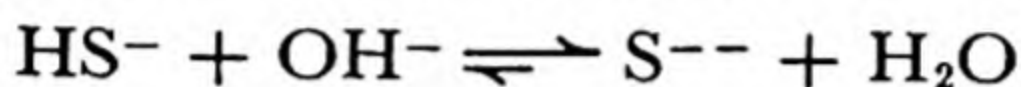
Solutions of the hydrosulfide are faintly basic and of the normal sulfide strongly basic, because of the basic nature of the anions and the effect of hydrolysis. The sulfides of sodium and potassium are prepared also by the reduction of the sulfates with carbon at high temperatures.

$$Na_2SO_4 + 4 C \longrightarrow Na_2S + 4 CO$$

These salts are used as laboratory reagents to furnish high concentrations of sulfide ions. Sodium sulfide is used industrially in the production of certain types of dyes and for the removal of hair from hides in preparation for tanning.

Polysulfides are formed by the reaction of the alkali metal sulfides with sulfur. The simplest of these salts is the disulfide.

$$S^{--} + S \rightleftharpoons S_2^{--}$$

The polysulfides are decomposed by acids with the evolution of hydrogen sulfide and the formation of finely divided sulfur in a suspension often called *milk of sulfur*.

$$S_2^{--} + 2 H^+ \longrightarrow H_2S + S$$
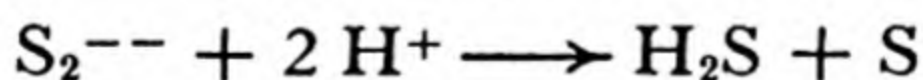
Calcium polysulfide, prepared by the reaction of sulfur with lime, is extensively used as lime-sulfur spray in vineyards and orchards.

The Sulfates. The sulfates of sodium, potassium, and ammonium are soluble and exhibit the general reactions of sulfate ions. Sodium and potassium sulfates are generally secured from natural deposits and as by-products in the formation of other substances.

Sodium Sulfate. **Na₂SO₄.** Some of the salt deposits in the southwestern part of the United States contain this substance in the form of the anhydrous salt, but the chief commercial source is the

salt-cake, obtained in the preparation of hydrochloric acid by the reaction of sulfuric acid with salt. At temperatures below 32.4°, sodium sulfate crystallizes from solution as the decahydrate, $Na_2SO_4(H_2O)_{10}$. This substance is known as *Glauber's salt*, because the alchemist Glauber prepared it in the seventeenth century and used it for medicinal purposes. At temperatures above 32.4°, the anhydrous salt crystallizes from solution. Unlike most salts, the solubility of the anhydrous salt decreases with rise in temperature. Sodium sulfate is used in the manufacture of glass and in the preparation of sodium sulfide, but its principal use is in the production of wood pulp by the sulfate process.

Potassium Sulfate. K_2SO_4. This substance is a constituent of the double salt, *schoenite*, $K_2SO_4MgSO_4(H_2O)_6$, and of the triple salt, *kainite*, $MgSO_4MgCl_2K_2SO_4(H_2O)_6$, found in the Stassfurt salt deposits. Potassium sulfate is prepared from schoenite by reaction with potassium chloride in the presence of a limited amount of water. Potassium sulfate is the least soluble of the salts involved and precipitates in the form of an anhydrous crystalline solid. This salt is used in the preparation of alums and as a fertilizer ingredient, especially for tobacco, since its presence in the product does not give an ash with a melting point as low as that caused by potassium chloride.

Ammonium Sulfate. $(NH_4)_2SO_4$. Ammonia, produced by the destructive distillation of coal, is absorbed in sulfuric acid with the formation of ammonium sulfate and is thus separated from the other volatile products of the process. The total quantity of ammonium sulfate obtained from this source depends primarily upon the production of coke in by-product coke ovens for use in the metal industries. Ammonium sulfate is also produced in large quantities from synthetic ammonia. The most extensive use of ammonium sulfate is in plant fertilizers. It is also used to some extent in the production of other ammonium salts.

Bisulfates and Pyrosulfates. Since the sulfuric acid molecule contains two replaceable atoms of hydrogen, it yields *hydrosulfates*, known as *bisulfates*, when an excess of sulfuric acid is used in the general acid reactions. The hydrosulfate may also be formed by the reaction of sulfuric acid with the normal salt.

$$SO_4^{--} + H_2SO_4 \rightleftharpoons 2\,HSO_4^{-}$$

When potassium hydroxide and sulfuric acid are mixed in equi-molal proportions, potassium hydrogen sulfate, $KHSO_4$, may be crystallized from the solution. Aqueous solutions of the hydro-sulfates are acidic because they contain the anion acid, HSO_4^-.

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$$
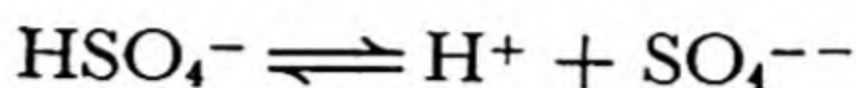
Potassium pyrosulfate, $K_2S_2O_7$, is formed by heating potassium hydrogen sulfate at moderate temperatures.

$$2\,KHSO_4 \longrightarrow K_2S_2O_7 + H_2O$$

The pyrosulfate decomposes when strongly heated with the formation of the normal sulfate and sulfur trioxide.

$$K_2S_2O_7 \longrightarrow K_2SO_4 + SO_3$$
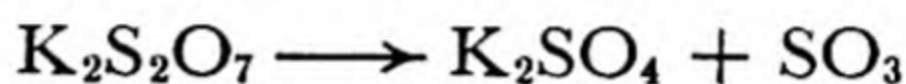
Fused pyrosulfates react with basic substances, since they contain an excess of the acidic oxide. Potassium pyrosulfate and ferric oxide react to form a mixture of normal sulfates when they are heated together.

$$3\,K_2S_2O_7 + Fe_2O_3 \longrightarrow 3\,K_2SO_4 + Fe_2(SO_4)_3$$
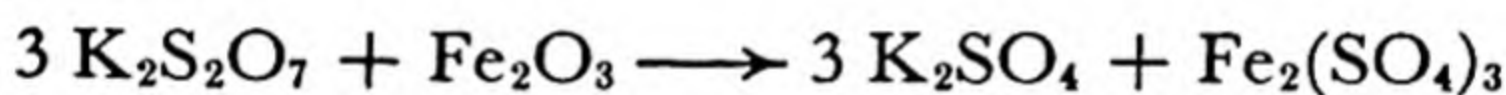
Sulfites and Hydrosulfites. The hydrosulfite or bisulfite is produced when a solution of sodium hydroxide is saturated with sulfur dioxide. The normal sulfite may be prepared by the reaction of the hydrosulfite with an equimolar quantity of sodium hydroxide.

$$OH^- + SO_2 \rightleftharpoons HSO_3^-$$
$$OH^- + HSO_3^- \rightleftharpoons SO_3^{--} + H_2O$$
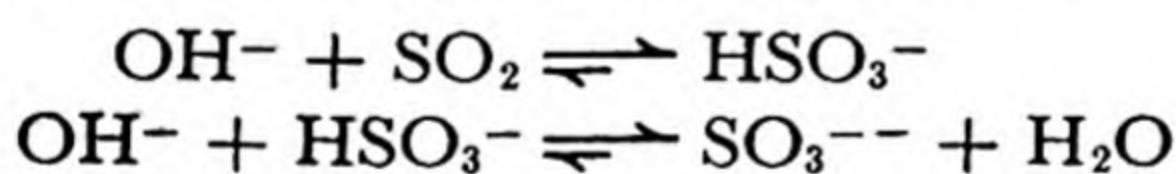
The sulfites are salts of the weak and unstable acid, sulfurous acid. Consequently, they react with stronger acids producing the acidic oxide, sulfur dioxide. This reaction is used as a convenient laboratory source of sulfur dioxide.

$$SO_3^{--} + 2\,H^+ \rightleftharpoons H_2O + SO_2 \uparrow$$
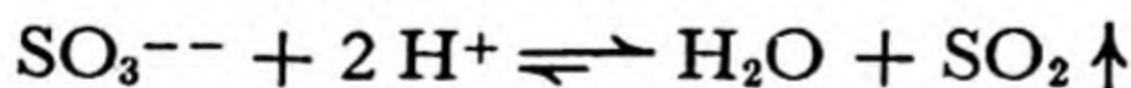
Sodium Thiosulfate. $Na_2S_2O_3$. This salt is prepared by the reaction of the sulfite with an excess of sulfur in hot alkaline solution.

$$SO_3^{--} + S \rightleftharpoons S_2O_3^{--}$$
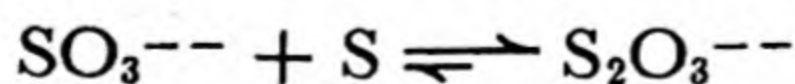
The thiosulfate ion decomposes in acidic solution, forming free sulfur and sulfur dioxide.

$$S_2O_3^{--} + 2\,H^+ \longrightarrow SO_2 \uparrow + S + H_2O$$
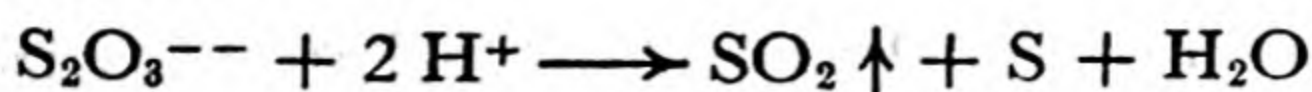
The pentahydrate, $Na_2S_2O_3(H_2O)_5$, is crystallized from solution. It is commonly called *hypo* from the older name, hyposulfite. This salt is used extensively in photography to dissolve unchanged silver salts from developed films and prints.

$$AgBr + 2 S_2O_3^{--} \rightleftharpoons Br^- + Ag(S_2O_3)_2^{---}$$
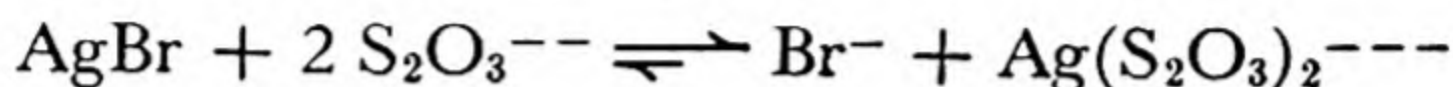
It is also used to remove the excess of chlorine from bleached materials in the textile and paper industries.

The Carbonates and Bicarbonates. The carbonates of sodium and potassium are highly important in chemical industry.

Sodium Carbonate. Soda Ash. **Na_2CO_3.** Deposits of sodium carbonate are found in Nevada and California, in Egypt, and in British East Africa. It is deposited in dry regions by the evaporation of lake water. Nevertheless, the major portion of the sodium carbonate used industrially is prepared from common salt.

Preparation of Sodium Carbonate. Before 1790, sodium carbonate was obtained exclusively from natural deposits and from the ashes of sea plants. The first industrial process for the production of sodium carbonate was developed by Le Blanc in 1790. This process was not able to withstand competition from the more efficient Solvay process, developed in 1866, and is no longer important.

A. Carbonating Tower.
B. Separation of Sodium Bicarbonate.
C. Ammonia Recovery.
D. Preparation of Ammoniacal Brine.
E. Circulating Pumps.
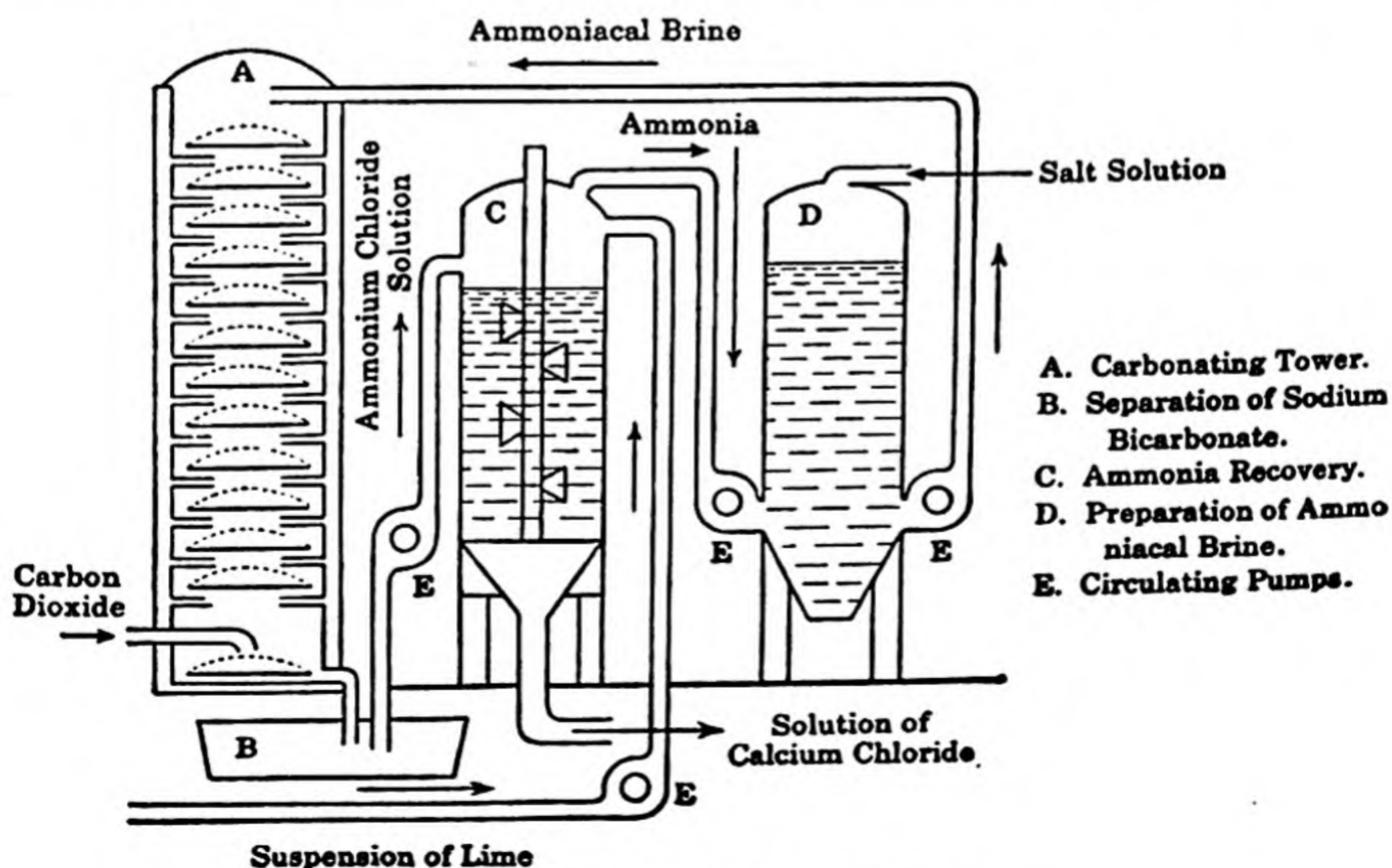
Fig. 111. Diagram of Solvay Process

The preparation of sodium carbonate by the *Solvay ammonia-soda process* depends on the precipitation of sodium hydrogen carbonate from solutions containing high concentrations of sodium and bicarbonate ions. The formation of sodium bicarbonate takes place in the carbonating tower. (Fig. 111.) This tower is divided by a number of perforated partitions and filled with a concentrated solution of sodium chloride saturated with ammonia. Carbon dioxide, forced in at the bottom of the tower, rises in small bubbles through the perforations in the partitions, and reacts with water and ammonia to form the bicarbonate.

$$NH_3 + H_2O + CO_2 \rightleftharpoons NH_4^+ + HCO_3^-$$
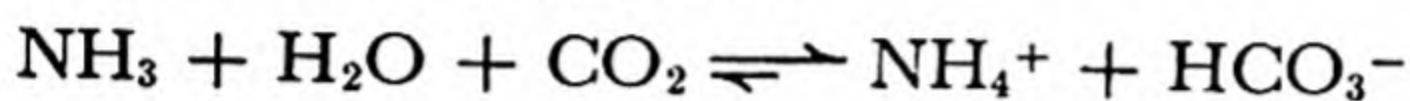
Sodium bicarbonate precipitates from this solution, because it is less soluble than the other salts involved.

$$Na^+ + HCO_3^- \rightleftharpoons NaHCO_3 \downarrow$$
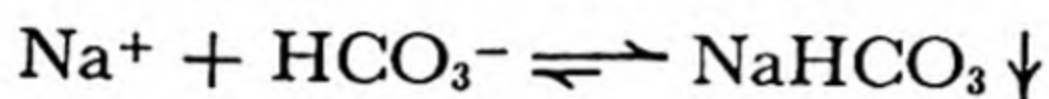
Precipitated sodium bicarbonate is separated from the solution and heated to form the normal carbonate, *soda ash.*

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \uparrow$$
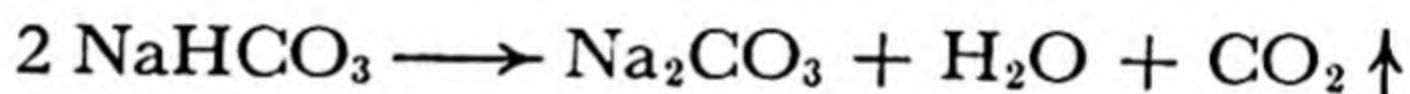
Carbon dioxide used in the process is produced by the thermal decomposition of limestone.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Ammonia is recovered from the ammonium salt by reaction with slaked lime and reabsorbed in saturated salt solution, thus repeating the cycle.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$2\,NH_4^+ + Ca(OH)_2 \longrightarrow 2\,NH_3 \uparrow + 2\,H_2O + Ca^{++}$$
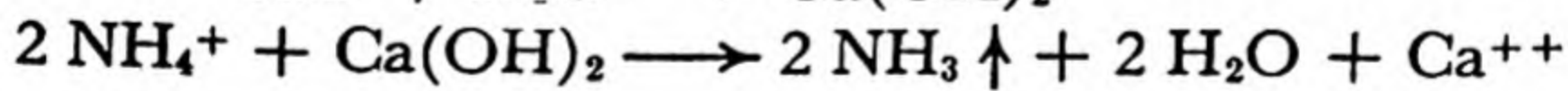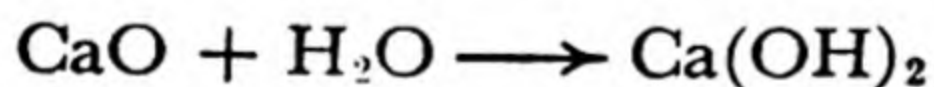
The reactions take place at about 35° so that fuel costs are low. There is but little handling of solid materials, making the labor costs low.

Properties and Reactions of Sodium Carbonate. This white crystalline solid dissolves readily in water. It crystallizes from solution as the decahydrate, $Na_2CO_3(H_2O)_{10}$, at temperatures below 30°. This hydrate, known as washing soda, has a solubility of about 23 g. in 100 g. of water at 25°. The heptahydrate, $Na_2CO_3(H_2O)_7$, is the stable form at temperatures of 30–35°, and the monohydrate, $Na_2CO_3(H_2O)$, is in stable equilibrium with the

saturated solution at temperatures above 35°. The decahydrate effloresces in dry air to form the monohydrate. The anhydrous salt is called soda ash.

Sodium carbonate exhibits the general reactions of carbonate ions, page 384. It reacts with an excess of a strong acid to produce carbon dioxide.

$$CO_3^{--} + 2\,H^+ \longrightarrow H_2O + CO_2 \uparrow$$

The hydrocarbonate is produced with low concentrations of hydrogen ions.

$$CO_3^{--} + H^+ \rightleftharpoons HCO_3^-$$
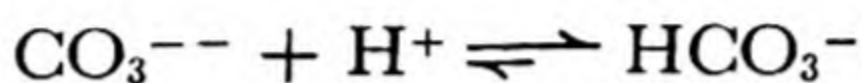
The hydrolysis of the carbonate yields a solution that contains both hydroxide and hydrocarbonate ions.

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-$$
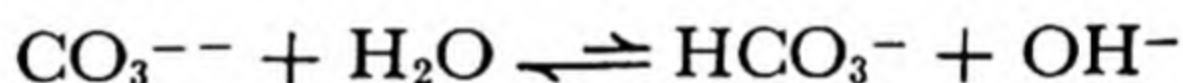
Solutions of sodium carbonate, consequently, react with metal ions to precipitate carbonates, hydroxycarbonates, or hydroxides, depending on the relative solubilities of these products. Solutions of calcium, strontium, and barium salts react with sodium carbonate to form slightly soluble carbonates.

$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3 \downarrow$$
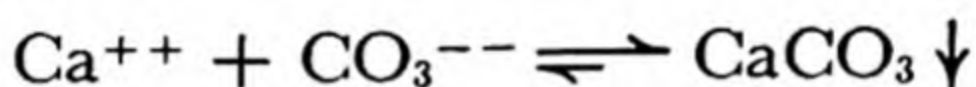
Soluble cupric, lead, and magnesium salts yield hydroxycarbonates. The equation in its simplest form is written:

$$2\,Cu^{++} + 2\,CO_3^{--} + H_2O \longrightarrow Cu_2CO_3(OH)_2 \downarrow + CO_2 \uparrow$$
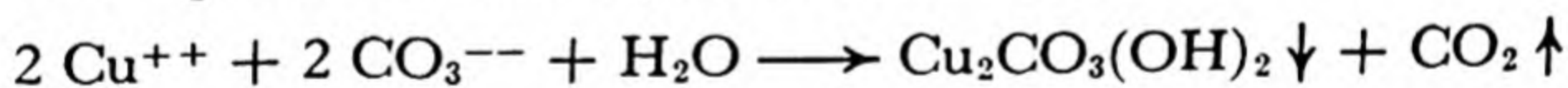
Aluminum, chromium, and ferric salts yield hydroxides or hydrated oxides in their reactions with sodium carbonate.

$$2\,Al^{+++} + 3\,CO_3^{--} + 3\,H_2O \longrightarrow 2\,Al(OH)_3 \downarrow + 3\,CO_2 \uparrow$$
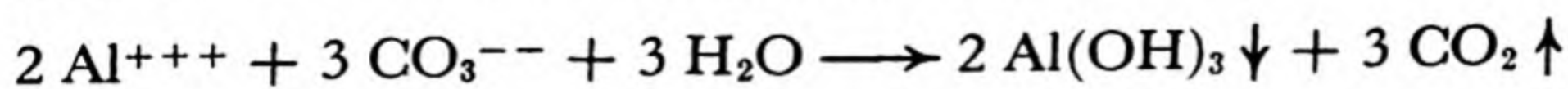
Uses of Sodium Carbonate. The production of sodium carbonate in 1943 in the United States was approximately 4,562,000 tons, about 4,380,000 tons by the ammonia-soda process. The estimated distribution of sodium carbonate is shown in Table 34.

Sodium Hydrogen Carbonate. Sodium Bicarbonate. **NaHCO₃.** This salt is the familiar *baking soda.* It is prepared by saturating a concentrated solution of the carbonate with carbon dioxide.

$$2\,Na^+ + CO_3^{--} + H_2O + CO_2 \longrightarrow 2\,NaHCO_3 \downarrow$$
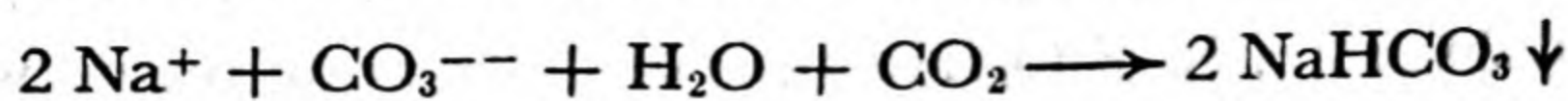
TABLE 34. ESTIMATED DISTRIBUTION [a] OF SODA ASH CONSUMED IN THE UNITED STATES (TONS)

Industry	1941	1942	1943
Glass	990,000	1,100,000	1,200,000
Soap	170,000	165,000	150,000
Caustic and bicarbonate	1,033,000	960,000	1,010,000
Other chemicals	800,000	840,000	950,000
Cleansers and modified sodas	70,000	80,000	85,000
Pulp and paper	155,000	145,000	155,000
Water softeners	70,000	80,000	95,000
Petroleum refining	23,000	18,000	20,000
Textiles	60,000	56,000	58,000
Nonferrous metals	150,000	260,000	450,000
Miscellaneous	225,000	230,000	370,000
Totals	3,746,000	3,944,000	4,543,000

This salt is used in making bread, in the preparation of baking powders, and in medicine. In order to leaven bread, minute bubbles of carbon dioxide are formed throughout the dough, causing it to rise. During the baking of the bread, the heat expands these minute gas bubbles, producing a light and porous product. In yeast breads, such as the bakers' loaf and rolls, carbon dioxide results from fermentation caused by yeast, but in breads made by the use of soda, an acid is added to react with the soda and form carbon dioxide.

$$H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2 \uparrow$$
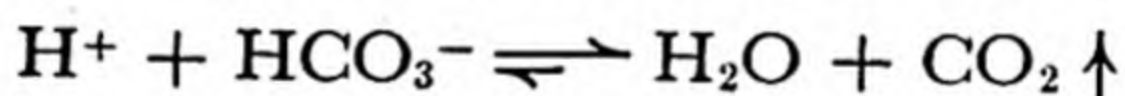
Sour milk contains lactic acid, so that it may be used for this purpose, but prepared baking powders are more extensively employed in making cake, biscuit, and similar leavened breads.

A baking powder is an intimate mixture of sodium hydrogen carbonate with a solid acid in reacting proportions. Suitable acidic substances for this purpose are potassium hydrogen tartrate, $KHC_4H_4O_6$, sodium dihydrogen phosphate, NaH_2PO_4, and sodium aluminum sulfate, $NaAl(SO_4)_2(H_2O)_{12}$, which hydrolyzes to liberate hydrogen ions. Starch and other inactive materials are added to prevent the substances becoming wet by the absorption of moisture from the air and to aid in obtaining a uniform distribution of the substances throughout the flour. The dry substances do not react with each other, but an acidic solution reacting with the bicarbonate is produced when water or milk is added.

$$HC_4H_4O_6^- + HCO_3^- \longrightarrow C_4H_4O_6^{--} + H_2O + CO_2$$
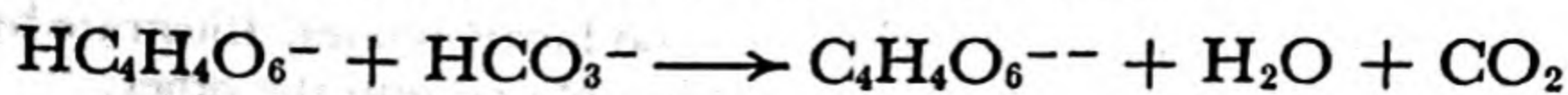
[a] *Chem. Met. Eng.* **51**, 2, 113 (1944).

The carbon dioxide produced in this reaction is adsorbed by the glutinous material in the flour, thus preventing its immediate escape into the air.

Potassium Carbonate. K_2CO_3. Potassium carbonate is present in wood ashes from which it may be extracted with water. Due to the relatively high solubility of potassium hydrogen carbonate, this salt cannot be prepared by a process similar to the Solvay process for soda. Potassium carbonate is usually prepared by heating potassium chloride solution with a suspension of magnesium carbonate and carbon dioxide under pressure. These substances react to form the slightly soluble mixed salt, potassium magnesium hydrogen carbonate.

$$2\,K^+ + 3\,MgCO_3 + CO_2 + H_2O \rightleftharpoons Mg^{++} + 2\,MgKH(CO_3)_2 \downarrow$$
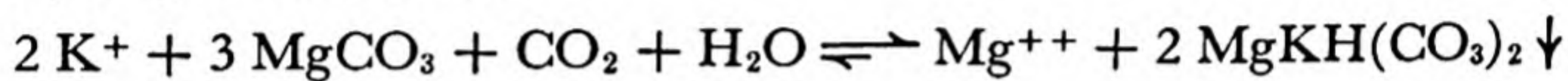
When this salt is heated in the presence of water, it decomposes with the evolution of carbon dioxide, leaving a residue of insoluble magnesium carbonate and a solution of potassium carbonate.

$$2\,MgKH(CO_3)_2 \longrightarrow 2\,MgCO_3 \downarrow + H_2O + CO_2 + 2\,K^+ + CO_3^{--}$$
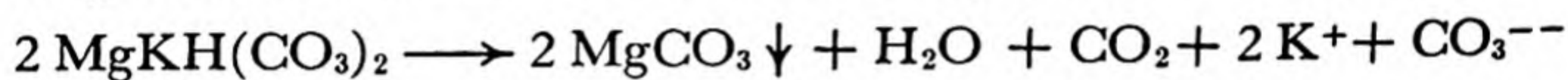
The solid is recovered from the solution by evaporation. Potassium carbonate, known as *pearl ash*, is used in the making of hard glass, soft soap, and many other substances.

EXERCISES

1. Represent by equations three reactions shown by chlorides.
2. What is the origin of the natural deposits of soluble salts? Account for the fact that such deposits are made up of strata of different composition.
3. Describe the production of potassium chloride from the brines of Searles Lake.
4. How are the bromides and iodides of sodium and potassium usually prepared? Why is this method used instead of separating these bromides directly from the salt deposits?
5. What are the two important sources of sodium nitrate?
6. Explain the production of potassium nitrate by the reaction of sodium nitrate with potassium chloride.
7. Represent by equations, derived by the oxidation number method, the reaction of potassium nitrate as an oxidizing agent in basic fusion with (a) arsenic, (b) sulfur, (c) arsenic trisulfide.
8. Write an equation to represent the reaction which occurs in the test for a nitrate in solution.
9. What is the relation between carbonates and bicarbonates? Illustrate by equations for reactions leading to the conversion of one into the other.
10. Represent by equations: (a) two reactions which may be used for the prepara-

tion of sodium hydrogen sulfate; (*b*) the effect of heating this salt; (*c*) the effect of heating the product formed in (*b*) with aluminum oxide.

11. Describe the production of sodium carbonate from sodium chloride, writing equations for all reactions involved in the process. Why is this process not suitable for the production of potassium carbonate?

12. Represent by equations the reaction of a solution of sodium carbonate with solutions of (*a*) barium chloride, (*b*) lead nitrate, (*c*) ferric chloride. Explain the formation of the precipitate you indicate in each instance.

13. Discuss the hydrolysis of sodium carbonate, indicating how the extent of hydrolysis may be increased and how it may be decreased. Explain these results.

14. Represent by equations the reactions indicated in the following successive changes: $NaCl \longrightarrow Na_2SO_4 \longrightarrow Na_2S \longrightarrow NaNO_3 \longrightarrow NaNO_2 \longrightarrow NaCl \longrightarrow NaOH \longrightarrow Na_2SO_3 \longrightarrow Na_2S_2O_3 \longrightarrow NaCl \longrightarrow NaHCO_3 \longrightarrow Na_2CO_3 \longrightarrow NaCN \longrightarrow Na_3PO_4 \longrightarrow Na_2HPO_4 \longrightarrow Na_2SO_4 \longrightarrow Na_2S \longrightarrow Na_2S_2 \longrightarrow NaCl.$

SUPPLEMENTARY READINGS

Badger, W. L., and E. M. Baker, *Inorganic Chemical Technology*, McGraw-Hill Book Company, Inc., New York, 1941, chaps. II, VI.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 2–4.

Furnas, C. C., *Rogers Manual of Industrial Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, chaps. 10, 13.

Teeple, J. C., *Industrial Development of the Searles Lake Brines*, Reinhold Publishing Corporation, New York, 1933.

Reichert, H. L., and H. W. Schulz, "Nitrate Fields of Chile," *Chem. Met. Eng.* **46**, 8, 464 (1939).

Turrentine, J. W., "Potash in War Production," *Chem. Eng. News* **21**, 1793 (1943).

"Salt Production," Pictured Flow Sheet, *Chem. Met. Eng.* **47**, 8, 565 (1940).

"Ammonia Soda Process," Pictured Flow Sheet, *Chem. Met. Eng.* **49**, 2, 134 (1942).

Chapter 26

THE METALLIC ELEMENTS

Some of the general properties of the metals have been discussed in preceding sections of this text. The metals are characterized by crystalline structures in which the atoms are closely packed in a compact material. In general metals are lustrous, have relatively high density and conductivity of heat and electricity. They also possess mechanical properties, such as varying degrees of ductility, malleability, and tensile strength. The crystals of metals are composed of particles arranged in structures that permit layers of atoms to slip over other layers without fracture, thus forming a body of altered external shape without change in the internal structure of the crystals. These properties vary greatly in metals, and the classification of a particular element as a metal is based on a consideration of all its properties rather than any single property. Sixty-eight of the elements have the physical properties of metals, and eleven of the remaining elements exhibit some metallic properties.

Reactions of the Metallic Elements. The most general reaction of the metals is the loss of electrons with the formation of positively charged ions. The force with which electrons are bound to an atom depends on its structure. Atoms containing small numbers of valence electrons usually release electrons in their reactions. The elements in Groups I, II, and III of the periodic system are metals, with the exception of boron. The atoms of the elements with high atomic numbers are larger than those with small numbers in the same group. Consequently, they loose electrons with greater activity, and some of the elements in the high-numbered groups are metallic, *viz.*, germanium, tin, and lead in Group IV, antimony and bismuth in Group V, and polonium in Group VI. The uncombined atoms of the transition elements, the elements in the subgroups, exhibit more or less metallic properties. The

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relationships among the transition elements, however, are irregular, because the electron shell within the valence shell is not complete.

Metals react with nonmetals, such as the halogens and sulfur, with the formation of binary salts. Metals with activities greater than hydrogen react with acids, such as the hydrohalic acids and dilute sulfuric acid, displacing hydrogen. Metals are also converted into their ions by reaction with strong oxidizing acids such as nitric acid. Some of the metallic elements undergo a transition in properties to assume nonmetallic character in their high oxidation states, *e.g.*, antimony, which yields antimonic acid when it reacts with nitric acid. Differences in the metallic elements are due primarily to differences in activity and in the valences of the ions which they produce.

Occurrence of Metals. Ores. The naturally occurring materials from which metals are extracted are *ores*. Some metals of low activity occur in the uncombined state. Such ores are known as *native ores*. Copper, silver, gold, and platinum are important metals obtained from native ores.

Metals occur most frequently in compound ores. There are several classes of *compound ores*, and some of the metals are obtained from more than one type of ore. *Oxide ores* are the most important sources of iron, aluminum, tin, and manganese. Copper and zinc are also obtained from oxide ores. *Sulfide ores* are used extensively in the production of copper, lead, zinc, mercury, and antimony. *The carbonate ores* of copper, zinc, magnesium, lead, and iron contribute to the supply of these metals. Calcium, barium, and strontium may be obtained from their carbonates, but at present these metals do not have extensive commercial uses. Calcium, barium, strontium, and magnesium also occur as sulfates. Few of the metals occur extensively as chlorides, but chlorides of sodium, potassium, and magnesium are important natural sources of these metals and of many of their compounds. Many of the metals occur more extensively in silicates than in any other compounds, but the silicates are not used extensively as ores, because of difficulties involved in the production of the metals.

Extraction of Metals from Ores. Different procedures are employed in the extraction of metals from their ores, depending on the nature of the ores. Many ores contain only small percentages

of the metal or its compounds, mixed with large proportions of rock. Such ores are usually concentrated before carrying out the metallurgical processes. It is not practical to secure complete separation between the metal compound and the rock in the concentration process. Hence, further separation of this material, known as *gangue*, must be made during the smelting of the ore. *The smelting of an ore* is the production of the metal in a molten state by means of a furnace process. Since metals occur in positive oxidation states in their compounds, reduction is required to produce the free metal. Products of smelting furnaces usually contain impurities, and *refining of the metal* is necessary for many uses.

The Concentration of the Ore. The concentration of an ore increases the percentage of the metal and decreases the percentage of gangue. The older methods of concentrating ores require the crushing of the ore in stamp mills and other types of crushing and grinding machinery, followed by washing out as much of the silicate rock as possible. The separation depends on differences in the densities of the crushed materials. The silicate rocks are less dense than most of the other metal compounds in the ore. Consequently, they do not settle out as quickly and may be floated away from more dense materials. This method is wasteful, for a considerable proportion of the desired materials may also be washed away. This method is not applied successfully to low grade ores. Nevertheless, concentration by washing is still employed for some ores, particularly native ores.

The modern method of ore concentration, used exclusively for sulfide ores and for some other classes of ores, is the *oil flotation process.* This process depends on the fact that the sulfide particles are selectively adsorbed by oil, and the silicate minerals are selectively wet by water. The ore is finely crushed and added to water containing suitable oils and emulsifying agents. The mixture is now agitated by a current of air and a froth is formed. The oily froth rises to the surface and carries the sulfide minerals, but silicates remain largely in the water layer. The froth is scraped off, the oil distilled out, and the concentrated ore is then carried through the smelting procedure. The water layer is discarded. The flotation process has made it feasible to work low grade ores which could not satisfactorily be handled by older methods of concentration.

Production of Metals from Native Ores. Several of the metals are obtained from important native ores, *e.g.*, copper, silver, and gold. The native metals occur in small percentages in rock. They are also found in sands resulting from the disintegration of rock. The production of the metal from such ores requires a process of separation. In addition to mechanical procedures for concentrating the ore, separation of the metal from gangue may be effected by smelting the materials in a furnace, and by leaching the metal from the ore, *i.e.*, dissolving the metal by reaction with suitable materials in solution.

Furnace processes for the separation of a metal from gangue require the use of a *flux* to react with materials which have high melting points, so as to form products that melt at the temperature of the furnace. Limestone is a suitable flux for ores containing silica and complex silicates. The fusible product resulting from the reaction of the flux with gangue is known as a *slag*. Although slag formation may involve many complex changes, the essential change is the reaction of acidic and basic materials with each other. The typical reaction may be shown by the following equation:

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
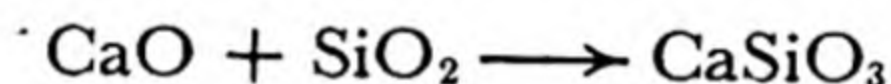
The smelting of native ores is extensively carried out in a *reverberatory furnace*. (Fig. 112.) In this type of furnace, flames from the burning fuel sweep over the charge on a shallow hearth. The charge introduced into the furnace is a mixture of concentrated ore and flux. The metal is melted and the flux and the silicate minerals react to produce a slag. The metal and the oxysalts of which slag is composed do not dissolve in each other, and the slag is less dense than the metal. Consequently,

Fig. 112. Diagram of a Reverberatory Furnace

the slag floats on the surface of the metal. The two liquid products may be tapped separately from the furnace or may be separated after being withdrawn. In addition, the reverberatory furnace is used for many other metallurgical processes.

The separation of the native metal from gangue may also be brought about in a *blast furnace*. (Fig. 113.) The solid charge, introduced from time to time at the top of the furnace, is a mixture containing the proper proportions of ore, flux, and coke to serve as fuel. A blast of hot air is blown in, near the base of the furnace, and coke burns fiercely generating the heat required for the process. Fusion of the metal and formation of slag take place as described above. The liquid products collect in the crucible at the base of the furnace and separate into two layers. They may then be tapped separately from the furnace. The blast furnace is designed to secure continuous operation.

Fig. 113. Diagram of a Blast Furnace

Metals may be separated from low grade ores by a *leaching process*. The crushed ore is extracted by the leaching solutions and undissolved materials are separated and discarded. Metals are then recovered from the compounds in solution by displacing them with more active metals, by electrolysis, and by other suitable procedures. Gold may be leached from native ores by reaction with sodium cyanide solution to form the complex cyanide ion.

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O \longrightarrow 4\,Au(CN)_2{}^- + 4\,OH^-$$
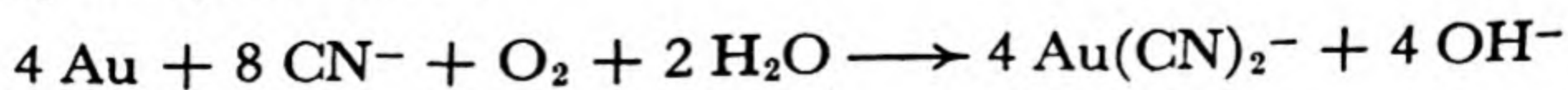
Gold may be displaced from this solution by reaction with zinc.

$$Zn + 2\,Au(CN)_2{}^- \longrightarrow 2\,Au + Zn(CN)_4{}^{--}$$
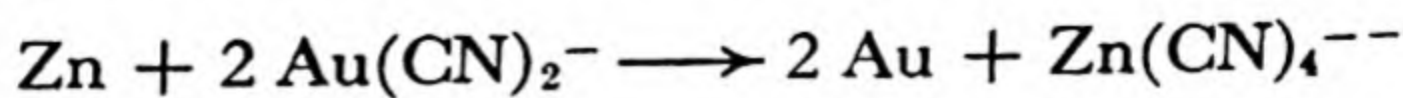
Production of Metals from Oxide Ores. The most extensively used method of producing metals from oxides, both those which occur as ores and those which are formed by burning and heating other ores, is *reduction with carbon*. The process for the production of iron and some of the other metals is carried out in a blast furnace,

with an excess of coke which serves as both fuel and reducing agent. A suitable flux is used to convert gangue into a fusible slag; and slag and metal are tapped from the furnace at different levels. Several of the metals are obtained by the reduction of their oxides with carbon in an electric furnace, *e.g.*, chromium, manganese, molybdenum, and vanadium. The excess of coke may be avoided in this process, since the energy is supplied by an electric current. There is less extensive reaction of the metal with carbon, forming the carbide, when restricted proportions of carbon are employed. A number of metals are produced in form of alloys with iron for use in the steel industry.

Some metals, active enough to combine extensively with carbon, may be produced by the reduction of their oxides with aluminum, a process known as *aluminothermy*. The pulverized oxide is mixed with aluminum powder, and heat to start the reaction is supplied by the reaction of an ignition mixture such as barium peroxide with magnesium powder. The reaction then proceeds vigorously with the evolution of large quantities of heat. This method may be used for the production of metals such as manganese, chromium, molybdenum, nickel, and cobalt. Metals produced in this manner are "carbon free," a condition desirable for the production of many alloys.

Reduction of oxides may also be brought about through the use of other reducing agents. Tungsten may be obtained by the reduction of its oxide with hydrogen at temperatures above 1000°. Magnesium is now produced by the reduction of its oxide with silicon.

Production of Metals from Carbonate Ores. The carbonates of magnesium and zinc and the hydroxy carbonates of copper are important ores of these metals. The production of metals from carbonate ores requires two metallurgical operations. The ores are first strongly heated in air to decompose the carbonates forming oxides. The oxides may then be reduced with carbon in a blast furnace or in an electric furnace. Barium, strontium, and calcium occur as carbonates, but these metals are not produced by reducing the oxides with carbon, because of the formation of carbides.

Production of Metals from Sulfide Ores. Sulfides are important ores of many of the metals, *e.g.*, copper, zinc, cadmium, lead,

mercury, silver, antimony, bismuth, and others. Several different processes are employed for the production of metals from sulfide ores. Usually two metallurgical processes are required. After the concentration of the ore, the first step in producing the metal is *roasting the ore*. Roasting of a sulfide ore consists in heating it in a current of air so that the sulfide is more or less completely oxidized. In the simplest procedure, sulfides are roasted to oxides that are then reduced. This procedure is followed in one of the methods for the production of zinc from its sulfide ore and in the production of bismuth, antimony, and certain other metals.

In some instances, the sulfide may also be converted into the sulfate by roasting at lower temperature with an excess of air. In a second method for the production of zinc, the sulfate formed in this manner is leached from the roasted ore, and the metal is deposited electrolytically from the solution.

In the production of some of the metals, particularly copper and lead, roasting is discontinued before all the sulfur has been oxidized. In such instances, partial roasting is carried out so as to simplify the steps required for the separation of undesired substances. This is discussed further in connection with copper.

Metals may be extracted more economically from low grade ores by leaching than by concentration of the ore and the use of smelting processes. Commonly, low grade sulfide ores of copper and silver are treated by a leaching process. The metals are recovered from the resulting solutions by electrolysis or by displacement.

The Electroformation of Metals. Metal ions are reduced by the gain of electrons at the cathode of an electrolytic cell. This process is carried out in the aqueous solution of the salts for the production of many of the metals.

There are a number of metals that cannot be prepared satisfactorily by the reduction of their oxides with carbon, because they are sufficiently active to react with the excess of carbon, thus producing carbides. Furthermore, some of these metals are so active that their ions cannot be reduced by electrolysis of aqueous solutions of their salts. A minimum electrical potential is required for the discharge of each variety of ion. (See page 236.) The discharge of hydrogen occurs at an electrode potential which is so

much lower than that required for the active metals — such as the alkali metals, the alkaline earth metals, and aluminum — that the ions of these metals are not discharged from *aqueous* solution. Metals of high activity are produced by the electrolysis of *fused* electrolytes. The fused chloride is commonly used as the electrolyte in the production of these metals, but aluminum is produced by electrolyzing the oxide dissolved in the anhydrous fused salt, sodium aluminum fluoride, Na_3AlF_6.

Electrorefining of the Metals. Metals produced in furnace processes are usually impure. Many ores contain other reducible substances besides the compounds of the metal for which the process is operated. The reduction of such substances often produces other metals found as impurities in the principal product. Small percentages of slag, held mechanically by the metal, and carbon dissolved in or combined with the metal are additional sources of impurities. Some impurities impart objectionable properties, while others have higher monetary value. Hence, the refining of many crude metal products is necessary. A number of metals are refined by electrolysis. The crude metal is made the anode, and a strip of the pure metal the cathode, in a cell containing a solution of a salt of the metal. Ions of the metal deposit at the cathode during the passage of the current, and simultaneously an equivalent number of ions dissolve from the anode. Metals of greater activity than the one being refined also dissolve at the anode, but do not deposit at the cathode, while metals of lower activity fail to enter into solution.

Alloys. Many of the metallic products, used extensively, are not single metals but alloys. *An alloy* is a material containing two or more metals intimately mixed or combined with each other. It is possible not only to modify the properties of metals by the formation of alloys but also to prepare metallic products possessing properties not exhibited by any single metal. In this way, a much wider range of choice is provided in the selection of metallic products for specific uses than offered by pure metals.

Types of Alloys. Alloys are usually prepared by melting metals together and allowing the melt to cool. There are several different types of alloys, some being homogeneous and others heterogeneous. The simplest type is that in which the two metals do not separate

when the melt solidifies. The crystals of the product contain both of the component metals in a homogeneous structure, known as a solid solution. In a second type, the cooling of the melt gives a homogeneous product that is not a crystalline solid. Such products are amorphous and are known as supercooled liquids. A third type of homogeneous alloy includes products resulting from the combination of the metals with each other to produce binary compounds.

Many alloys are heterogeneous in structure. Usually, during the cooling of the liquid melt — a solution of the two metals in each other — the saturation point of one of the metals is reached before the other, and it begins to crystallize as further cooling proceeds. This causes an increase in the concentration of the other metal with corresponding reduction in the freezing point. As these changes continue, the temperature and concentration become adjusted so that both metals crystallize together without further change in either proportions or temperature until the melt has completely solidified. The temperature at which the final crystallization of the heterogeneous mixture occurs is the lowest temperature for a liquid phase to exist in the system. This temperature is known as the *eutectic temperature;* and the mixture which solidifies at this temperature is the *eutectic mixture.*

EXERCISES

1. How are the general properties of metals related to their crystalline structures?
2. Discuss the general reactions and activities of the metals in terms of their atomic structures.
3. What is an ore of a metal? Name the common classes of ores, and give examples of metals produced from each of these classes.
4. Outline the procedure for the production of the metal in each of the principal classes of ores.
5. What is the meaning of the following terms: gangue, flux, slag, smelting an ore, refining a metal, reverberatory furnace, blast furnace?
6. What is meant by concentration of an ore? What two methods are extensively used for this purpose?
7. How are the metals of high activity commonly produced? Why is this method selected?
8. What method is widely employed in refining metals? What must be done to arrange the materials for refining metals by this method?
9. What are alloys? How are they usually prepared?

SUPPLEMENTARY READINGS

Hayward, C. R., *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1929.

Hayward, C. R., "Extraction of Metals from Ores," *J. Chem. Education* **20**, 29 (1943).

Chapter 27

THE ALKALINE EARTH METALS

The elements in Group II of the periodic system are *beryllium*, *magnesium*, *calcium*, *strontium*, *barium*, and *radium*. The atoms of these elements contain two valence electrons, and in each instance, the kernels of the atoms have the electronic structure of the next lower inert gas. The elements, with the exception of beryllium, are actively metallic, and their activity increases in the order of the atomic numbers.

Occurrence of the Metals. The alkaline earth metals do not occur naturally in uncombined state. The most important of the beryllium compounds found in nature is *beryl*, $Be_3Al_2(SiO_3)_6$. This silicate is the gem *emerald* when colored green by the presence of chromium compounds. Magnesium occurs in the chloride and the sulfate of salt beds in the form of the carbonates *magnesite*, $MgCO_3$, and *dolomite*, $MgCO_3CaCO_3$, and in complex silicates such as *talc*, $Mg_3H_2(SiO_3)_4$, and *asbestos*, $CaMg_3(SiO_3)_4$. Important natural compounds of calcium, in addition to dolomite, are *calcite*, $CaCO_3$, in limestone and marble, *gypsum*, $CaSO_4(H_2O)_2$, *phosphorite*, $Ca_3(PO_4)_2$, and *fluorspar*, CaF_2. The sulfates are the most important natural compounds of strontium and barium, *celestite*, $SrSO_4$, and *barite*, $BaSO_4$, respectively, but carbonates also occur, *strontianite*, $SrCO_3$, and *witherite*, $BaCO_3$, respectively.

Production of the Alkaline Earth Metals. These metals, like the alkali metals, are prepared by the electrolysis of fused compounds, usually the chlorides. Beryllium and magnesium are also prepared by the reduction of their oxides. The first step in the production of these metals by the electrolytic process is the preparation of the anhydrous chloride. The hydrated salts are obtained by crystallization from solution. The chlorides of barium and strontium may be dehydrated by moderate heating, but the hydrated chlorides of beryllium, calcium, and magnesium decompose to

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form the oxides when they are heated. Consequently, special procedures are required for the preparation of the anhydrous salts for use in electrolysis. The general method for the production of all these metals is the same, but there are differences in some of the operating details. Magnesium is the most important of these metals. Smaller quantities of beryllium and calcium are produced for industrial use, but barium and strontium have no important industrial uses at this time.

Production of Magnesium. The production of metallic magnesium increased from a few hundred tons in 1937 to an estimated rate of 300,000 tons in 1943, while the price has decreased to about 22.5 cents per pound. Several new processes have been developed to supplement the production by the electrolytic process, *viz.*, reduction of the oxide with carbon, and reduction of the oxide with silicon. However, the electrolytic process is still the most extensively employed.

The Electroformation of Magnesium. Magnesium chloride for the electrolytic process may be obtained from salt well brines, salt deposits, sea water, and from naturally occurring carbonate and oxide. *The Michigan salt well brines* contain sodium, magnesium, calcium, chloride, bromide, and small proportions of other ions. The proportions of these ions are equivalent to an average composition of 14 per cent of sodium chloride, 9 per cent of calcium
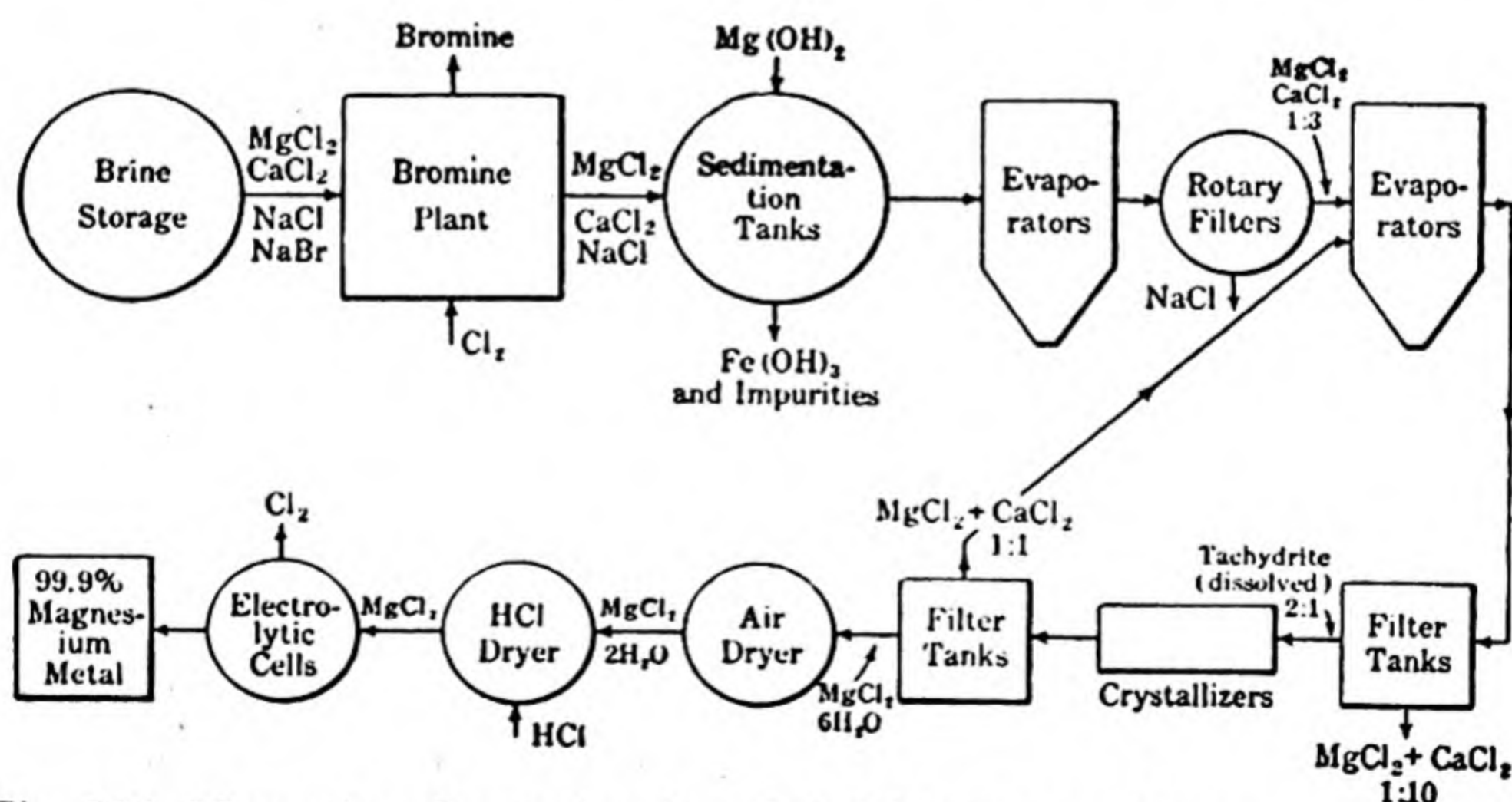
Fig. 114. Magnesium Production from Salt Well Brines. (Courtesy of the Dow Chemical Company.)

chloride, 3 per cent of magnesium chloride, and 0.15 per cent of bromine, although some of the brines contain magnesium chloride up to 10 per cent. The steps in the production of anhydrous magnesium chloride are shown in outline form in Fig. 114. Bromine, an important product of the process, is displaced by chlorine. The hydroxides of iron and other metals, less active than magnesium, are precipitated by the addition of a suspension of magnesium hydroxide. The solution is then evaporated to crystallize most of the common salt. Further evaporation with the proper regulation of ion concentrations and temperatures causes the crystallization of the double salt, tachydrite, $(MgCl_2)_2CaCl_2(H_2O)_{12}$, from a mother liquor containing magnesium and calcium ions in a ratio of one to ten. The double salt is dissolved in water, and magnesium chloride hexahydrate, $MgCl_2(H_2O)_6$, is crystallized, leaving a solution containing the two metal ions in a one to one ratio. This solution contains approximately 50 per cent of the magnesium in the original brine. It is returned to the process, as indicated, to aid in the regulation of the ion concentrations for the precipitation of the double salt. The hexahydrate may be converted into the dihydrate by heating in air at a controlled temperature. Dehydration is completed by heating the dihydrate in a current of hydrogen chloride gas which serves to prevent hydrolysis.

The electrolysis of the fused chloride takes place in an iron cell which is heated to maintain the necessary temperature. Graphite anodes project downward into the cell. Iron cathodes are placed on opposite sides of the row of anodes. Magnesium is liberated at the cathode and chlorine at the anode. The cathodes are so constructed that small drops of the metal are deflected as they rise and pass through openings in the cathode into the space back of it, where the liquid metal collects. Contact with chlorine is avoided in this manner. The metal in the reservoir is protected from atmospheric oxidation by a film of the electrolyte. The direct product of the cells has a purity of approximately 99.9 per cent, and subsequent refining is not necessary.

The production of magnesium from sea water differs from the procedure just described in the source of magnesium chloride. Sea water contains approximately 0.13 per cent of magnesium. Magnesium hydroxide is precipitated by reaction with calcium hydroxide and

converted into the chloride by reaction with hydrochloric acid. The chloride is then crystallized from solution, dehydrated, and electrolyzed. The steps in the process are shown in outline in Fig. 115.
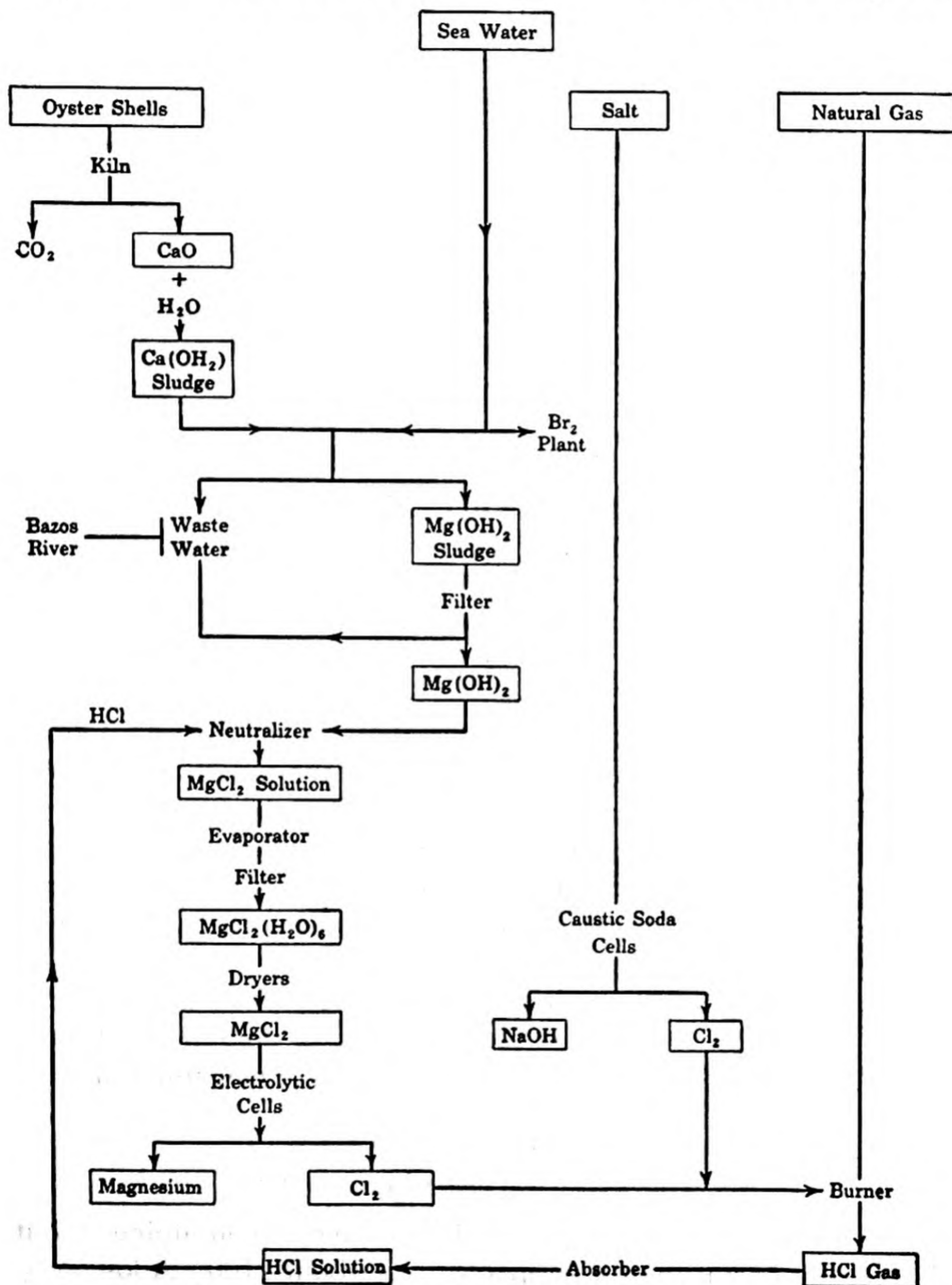
Fig. 115. Outline — Production of Magnesium from Sea Water

The electrolytic production of magnesium from the carbonate, *magnesite*, and the oxide, *brucite*, requires the formation of the anhydrous chloride. The carbonate is converted into the oxide by thermal decomposition.

$$MgCO_3 \longrightarrow MgO + CO_2$$
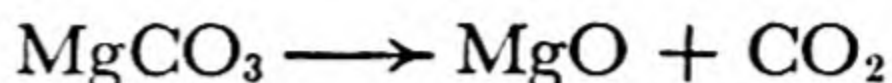
The anhydrous chloride may be formed by the reaction of chlorine with a mixture of magnesium oxide and carbon at a temperature of 800–1000°.

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$
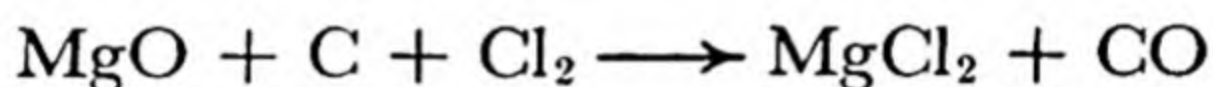
This is one of the important sources of the metal.

Electrothermal Production of Magnesium. *Magnesium may be prepared from the oxide by reduction with carbon* at high temperatures. The reduction is carried out in an electric furnace at a temperature of 2000–2100°.

$$MgO + C \rightleftharpoons Mg + CO$$
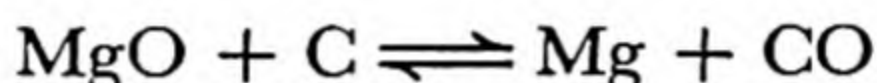
Gaseous magnesium and carbon monoxide are volatilized from the furnace at this temperature. If the gases are allowed to cool slowly, the reverse reaction takes place to such an extent that no practical production of the metal is obtained, but metallic magnesium may be condensed by cooling the gases quickly. The cooling of the vapor must be done through the use of gases that do not react with magnesium. The product obtained in this manner is a dust containing 60–65 per cent of magnesium mixed with the oxide and carbon. This mixture is heated at a temperature of about 750° in a retort under reduced pressure, and magnesium is distilled and condensed to a crystalline product with a purity of about 99.97 per cent. The essential steps in this process are indicated in outline in Fig. 116.

Magnesium may also be produced from the oxide by reduction with silicon. In this process, known as the Pidgeon process, dolomite is decomposed by heat to form a mixture of the oxides of calcium and magnesium.

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$MgCO_3 \longrightarrow MgO + CO_2$$
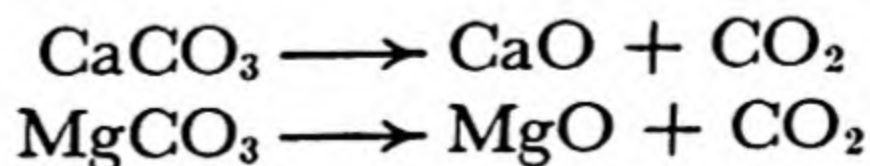
The oxide mixture is heated with ferrosilicon containing about 75 per cent of silicon at a temperature of about 2100°. A low pressure is maintained and magnesium is distilled from the retort.

$$2\,MgO + 2\,CaO + Si \longrightarrow 2\,Mg \uparrow + Ca_2SiO_4$$
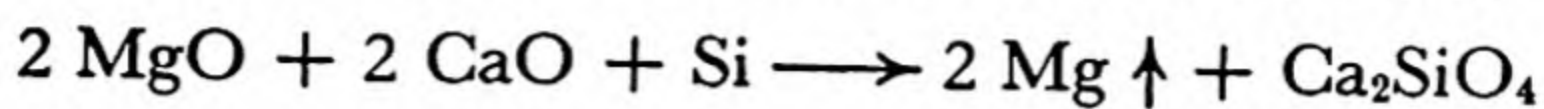
The reaction of magnesium oxide with silicon is reversible, but the reaction of calcium oxide with the silicon dioxide and the distillation of the magnesium cause the completion of the reaction. Mag-
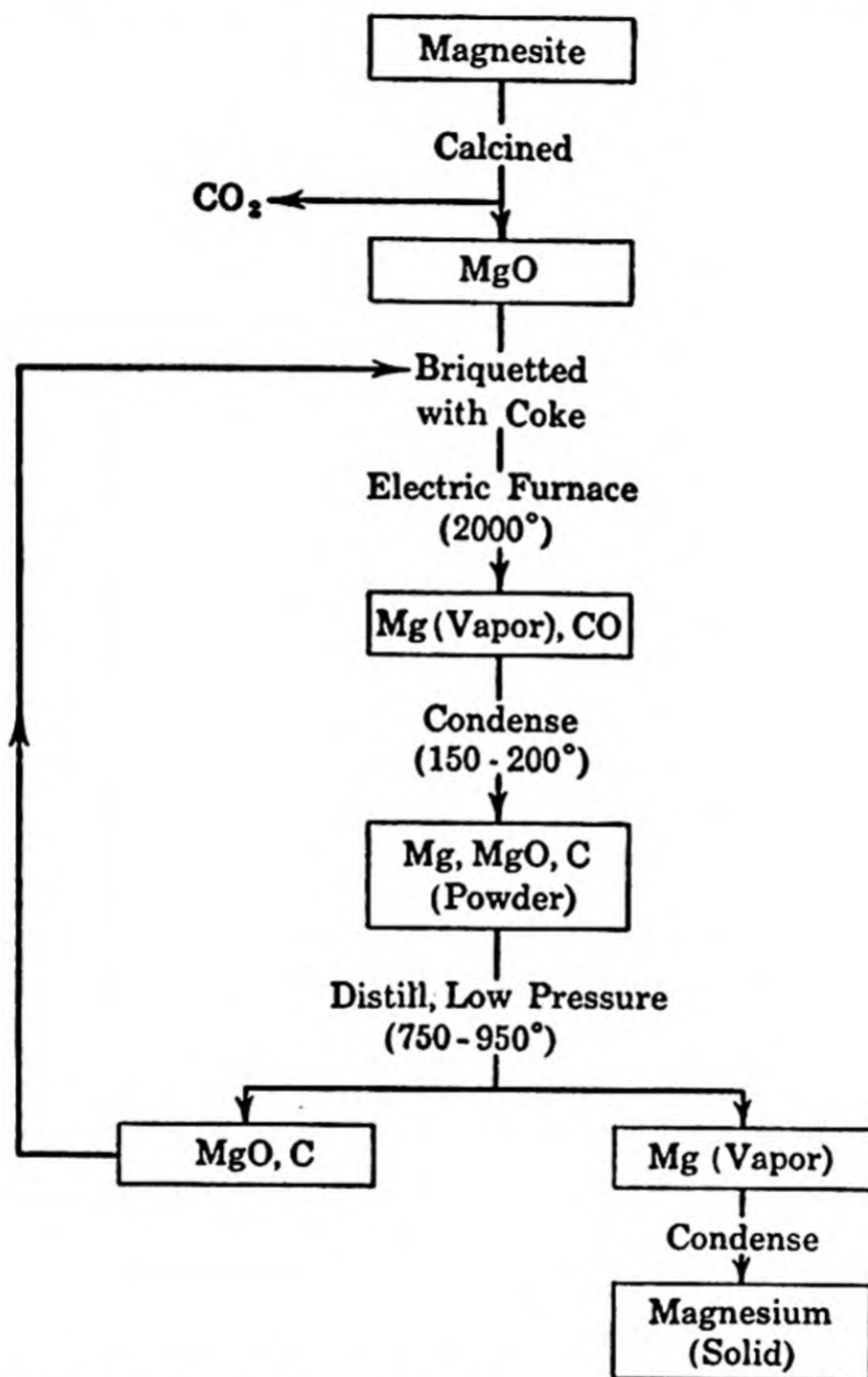
Fig. 116. Outline — Production of Magnesium by an Electrothermal Process

nesium of a high degree of purity is the direct product of this process.

The Production of Beryllium. *Beryl*, the complex silicate of beryllium and aluminum, $Be_3Al_2(SiO_3)_6$, is not easily decomposed by acids. Nevertheless, the product, formed when the mineral is melted and then suddenly cooled by pouring it into cold water,

reacts with sulfuric acid, producing the sulfates of beryllium, aluminum, and such other metals as may be present in the ore. Beryllium sulfate may be recovered from the solution and decomposed by heat. The oxide is then heated with carbon in an atmosphere of chlorine to form the anhydrous chloride. Metallic beryllium may be prepared from the anhydrous chloride by reduction with sodium or magnesium and by electrolysis. Metallic beryllium is often prepared in the form of a master alloy with copper by reduction of the mixed oxides with carbon or with hydrogen.

Properties of the Metals. These elements are characterized by the properties usually associated with metals. They are good conductors of heat and electricity, and the freshly cleaned surfaces have silvery white luster. They possess varying degrees of malleability, but are somewhat brittle at ordinary temperatures. Beryllium is very hard but barium is soft. Beryllium has low ductility. Several of the properties of the elements are listed in Table 35.

TABLE 35. PROPERTIES OF THE ALKALINE EARTH METALS

Property	Be	Mg	Ca	Sr	Ba
Atomic weight	9.02	24.32	40.08	87.63	137.36
Atomic number	4	12	20	38	56
Isotopes	9	24, 25, 26	40, 44, 42, 43, 46, 48	84, 87, 90	138, 136, 134, 137, 135, 132
Electron structure	2, 2	2, 8, 2	2, 8, 8, 2	2, 8, 18, 8, 2	2, 8, 18, 18, 8, 2
Melting point (° C.)	1350	651	810	800	850
Boiling point (° C.)	1530	1120	1240	1150	1140
Density at 20°, g. per ml.	1.85	1.74	1.55	2.6	3.5

Reactions of the Metals. The metals of this group burn in air with the formation of an oxide. Barium yields the peroxide. When they burn in air, they combine to some extent with nitrogen to form the nitride. The metals lose electrons actively and stand high in the electromotive series of the metals. Beryllium and magnesium do not react perceptibly with water because of the presence of a protective coating of oxide or hydroxide. Magnesium displaces hydrogen rapidly from hot water containing ammonium chloride, because magnesium hydroxide dissolves under these conditions and a fresh surface of the metal is continually exposed.

$$Mg + 2 H_2O \longrightarrow Mg(OH)_2 \downarrow + H_2$$
$$Mg(OH)_2 + 2 NH_4^+ \longrightarrow Mg^{++} + 2 NH_3 + 2 H_2O$$
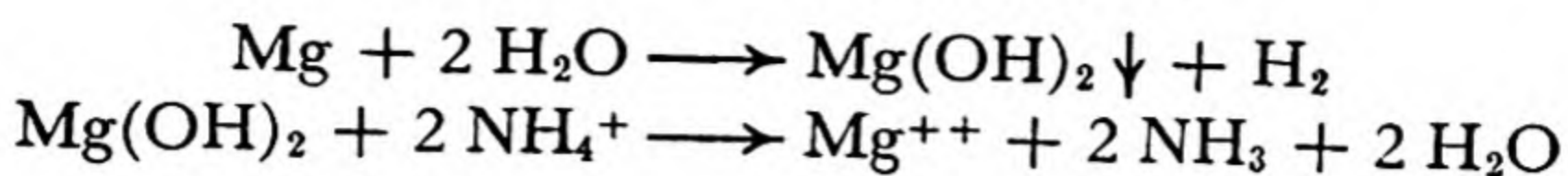
Similarly, beryllium reacts with water containing sodium hydroxide in solution, because the hydroxide of beryllium is amphoteric and is dissolved by the basic solution.

$$Be + 2 H_2O \longrightarrow Be(OH)_2 \downarrow + H_2$$
$$Be(OH)_2 + 2 OH^- \longrightarrow Be(OH)_4^{--}$$
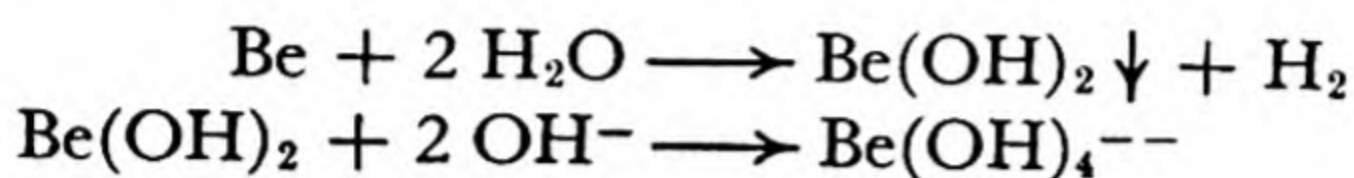
The metals also displace hydrogen from acids and exhibit the usual reactions of metals with nonmetals, forming stable salts by direct union with the halogens and sulfur. In all of these reactions the metals form simple divalent positive ions. They also react with less active nonmetals, such as phosphorus and carbon, to form binary compounds. The atoms of beryllium are the smallest and of radium the largest in the group. Consequently, the valence electrons of beryllium are held most firmly, of radium least firmly, and the others are intermediate. Therefore, beryllium is the least active member of the group, and there is a regular increase in activity from metal to metal in the order of increased atomic numbers, and radium is chemically the most active member of the group.

Uses of the Metals. Magnesium is the only metal in this group with extensive commercial uses. The principal use of the metal is in structural products. Approximately 95 per cent of the annual production is used in making alloys. Most of the metals with low melting points form alloys with magnesium, but in general, metals with melting points above 1200° dissolve in melted magnesium to a limited extent only. Beryllium, however, does not alloy with magnesium, while nickel and silicon alloy readily with magnesium, and manganese to a limited extent. Magnesium based alloys, containing 10–12 per cent of aluminum together with small percentages of zinc and manganese as alloying elements, are light and have high tensile strength. They may be cast, rolled, drawn, and forged. They are employed extensively in aircraft construction. An alloy containing magnesium, copper, cadmium, and aluminum is used in pistons. A process was discovered a few years ago for the treatment of magnesium alloys with sodium hydroxide under pressure to form a dense adherent film which resists corrosion

and protects the metal. Protective coatings are also produced by electrolytic oxidation at the anode in a solution containing chromic acid and various salts.

Because of its high chemical activity, magnesium is used in incendiary shells and as a casing for incendiary bombs. It is also used in flares for signaling and for illuminating landing fields and military objectives. The metal is used as a deoxidizing and desulfurizing agent in the refining of certain metals, especially nickel and its alloys. Magnesium ribbon is used for the removal of residual gases from radio tubes, since the hot metal combines with both oxygen and nitrogen.

The chief use of *beryllium* is in the production of its alloys with copper. These alloys are hard and strong and may be tempered. They are particularly important in springs, because they possess high elasticity and great endurance. The properties of the copper-beryllium system are affected to a great extent by the presence of other metals. Beryllium-nickel-copper alloys, containing 2.25 per cent of beryllium, have tensile strengths above 200,000 lb. per square inch. The present high price of the metal prevents more extensive applications. Beryllium alloys have come into use in the manufacture of parts of airplane engines.

Calcium has limited industrial uses. Its cost is too great to permit general use in steel making, but it is used as a deoxidizing agent for stainless steel and other special alloy steels. The metal is also used as a reducing agent for the production of rare metals, such as titanium, vanadium, and uranium.

COMPOUNDS OF THE ALKALINE EARTH METALS

The metals of this group yield simple positive ions that form salts with many of the anions. Many of these salts are hydrated. The ions of beryllium and magnesium become hydrolyzed to produce acidic solutions.

$$Mg^{++} + H_2O \rightleftharpoons MgOH^+ + H^+$$
$$Be^{++} + H_2O \rightleftharpoons BeOH^+ + H^+$$
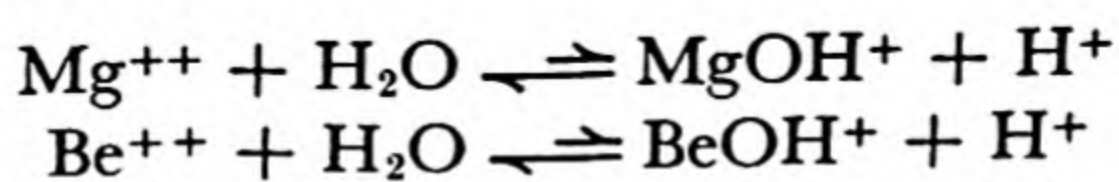
The ions of the other metals in this group are stable toward hydrolysis. Beryllium ions yield the hydroxide complex, $Be(OH)_4^{--}$,

with an excess of hydroxide ions, but the other ions in this group do not readily form complex ions.

The Oxides and Hydroxides. *Magnesium oxide*, **MgO**, is prepared by the thermal decomposition of the carbonate.

$$MgCO_3 \longrightarrow MgO + CO_2$$
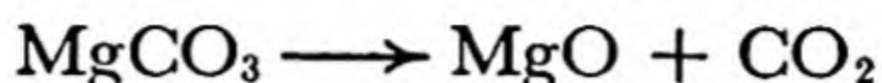
This oxide is stable toward heat and is highly infusible. Because of these properties, it is used in the manufacture of firebrick. Mixed with asbestos, it is used as a covering for steam pipes and hot water pipes to minimize heat losses. The reaction of magnesium oxide with acidic substances, such as silicon dioxide and phosphorus pentoxide, to form a slag is important in the steel industry.

$$MgO + SiO_2 \longrightarrow MgSiO_3$$
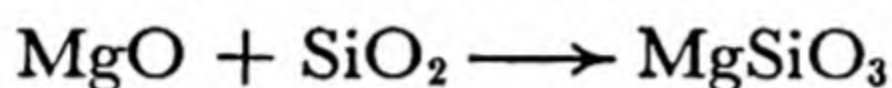
Instead of magnesium oxide alone, a mixture of magnesium oxide and calcium oxide, resulting from the thermal decomposition of dolomite, $MgCO_3CaCO_3$, is employed extensively in the steel industry. Magnesium oxide is also used in compounding and vulcanizing of rubber and as an absorbent in the production of dynamite.

Fig. 117. *Pressures of Carbon Dioxide in Equilibrium with Calcium and Barium Oxides*

Calcium oxide, quicklime, **CaO,** is prepared industrially by heating limestone. The decomposition of limestone is an endothermic reaction which is reversible.

$$CaCO_3 \rightleftharpoons CaO + CO_2 - 42,900 \text{ cal.}$$

The pressure of carbon dioxide in equilibrium with the oxide is about 2.3 mm. at 600°, 168 mm. at 800°, and 760 mm. at 910°. (Fig. 117.) Consequently, temperatures above 910° would be necessary for the complete decomposition of calcium carbonate in a retort furnace. Complete decomposition may be brought about at lower temperatures by blowing a current of an inert gas over the heated limestone to sweep away carbon dioxide and keep its partial pressure below the equilibrium pressure. The modern lime

kiln is a large tower approximately 100 ft. in height and 10 ft. in diameter. (Fig. 118.) Limestone, fed into the hopper at the top, passes slowly down through the heated portion of the kiln. The flame of the burning fuel sweeps in from the side, causing the decomposition of limestone. There is a second hopper below the fire level in which the lime is allowed to cool before it is dumped into cars.

Calcium oxide is a white solid that melts at 2572°. The solid becomes incandescent and emits a brilliant white light when it is heated intensely. The oxide is stable toward heat and does not decompose in the electric arc. It is an active basic oxide reacting with water and with acids. It also reacts with acidic oxides at higher temperatures.

Fig. 118. Vertical Section of a Shaft Lime Kiln

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$CaO + 2 H^+ \longrightarrow Ca^{++} + H_2O$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$
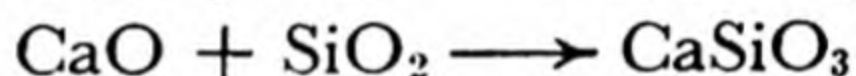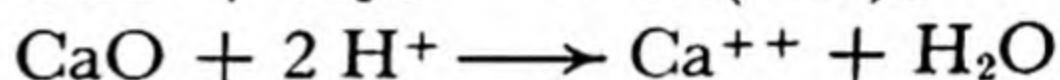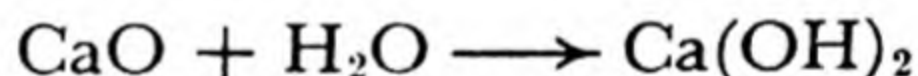
The oxide becomes airslaked when it is exposed to air containing water and carbon dioxide, forming a mixture of the hydroxide and carbonate. The carbide is formed by strongly heating a mixture of the oxide and carbon.

$$CaO + 3 C \longrightarrow CaC_2 + CO$$
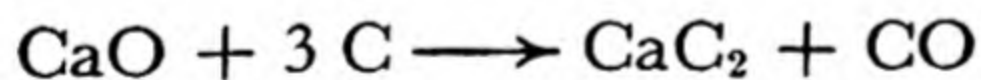
Several million tons of calcium oxide are produced annually in the United States. Large quantities of this oxide are employed in the production of slaked lime, calcium hydroxide, for use in plaster and mortar and for many other purposes.

Calcium hydroxide, slaked lime, Ca(OH)₂, is prepared by the reaction of the oxide with water, a process known as slaking lime. The reaction is exothermic.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15,300 \text{ cal.}$$
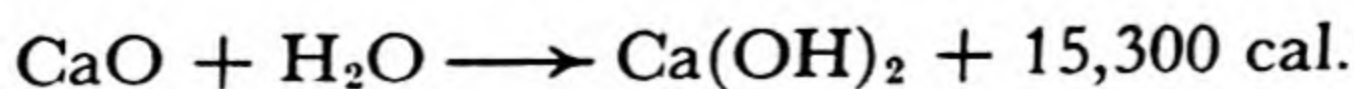
The solid may be decomposed by heating it to high temperatures. Calcium hydroxide is a white powder with low solubility, 0.17 g. in 100 g. of water at 20°. The solubility of this substance decreases

with rise in temperature. It is a strong base, the dissolved material being ionic

$$Ca(OH)_2 \downarrow \rightleftharpoons Ca^{++} + 2\,OH^-$$
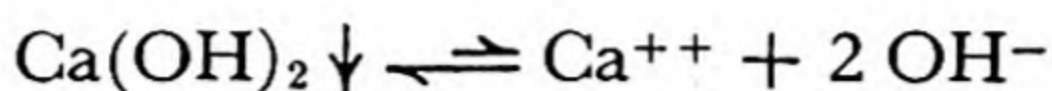
Calcium hydroxide is used extensively in industry, *e.g.*, in the preparation of ammonia from ammonium salts and of sodium and potassium hydroxides from their carbonates, in agriculture to neutralize soil acidity, in making mortar and plaster, in sugar refining, and for a number of additional purposes. The use of calcium hydroxide in sugar refining depends on its reaction with sucrose to form an insoluble saccharate. This precipitate is separated from the impurities that remain in the solution, and is then suspended in water and decomposed by the action of carbon dioxide. Calcium carbonate precipitates, leaving a solution of sugar. Solutions of calcium hydroxide, known as *limewater*, are used medicinally to counteract excessive acidity of the contents of the stomach. Calcium hydroxide is used as a laboratory reagent in testing for the presence of carbon dioxide. This gas is absorbed in solutions of calcium hydroxide with the formation of a white precipitate.

$$Ca^{++} + 2\,OH^- + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$
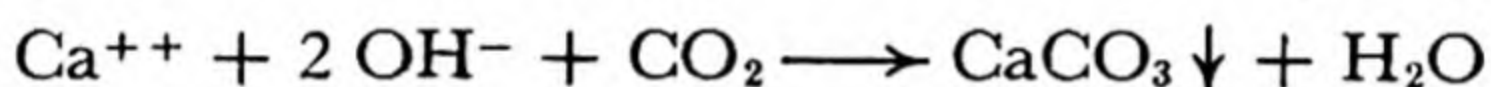
Mortar is a mixture of slaked lime, sand, and water. As the mixture dries, the lime crystallizes and cements the particles of sand together and to the brick or stone. There is also some combination with carbon dioxide of the air, but this seems to be of minor importance in the setting of mortar, for only a superficial change occurs over a period of years.

Strontium hydroxide, **Sr(OH)₂,** may be prepared by heating the carbonate in a current of steam.

$$SrCO_3 + H_2O \longrightarrow Sr(OH)_2 + CO_2 \uparrow$$
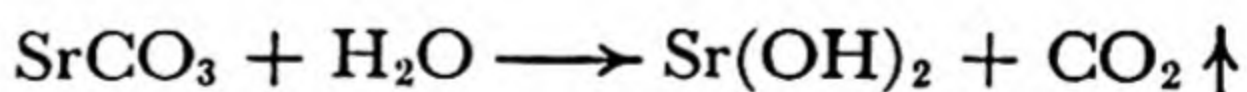
This reaction is equivalent to the decomposition of the carbonate into the oxide, followed by the reaction of the oxide with water. The direct reaction of the carbonate with steam takes place at a lower temperature, because of the low pressure of carbon dioxide maintained and the large amount of heat evolved in the formation of the hydroxide. Strontium hydroxide is also used in sugar refining.

Barium oxide, **BaO,** is produced by the decomposition of its carbonate. Barium carbonate is more stable toward heat than cal-

cium carbonate, and the partial pressure of carbon dioxide is lower at each temperature than in the equilibrium system of carbon dioxide with calcium oxide. The reverse reaction is prevented by mixing coke with barium carbonate, because carbon dioxide is reduced to the monoxide.

$$BaCO_3 \rightleftharpoons BaO + CO_2$$
$$CO_2 + C \longrightarrow 2\,CO \uparrow$$
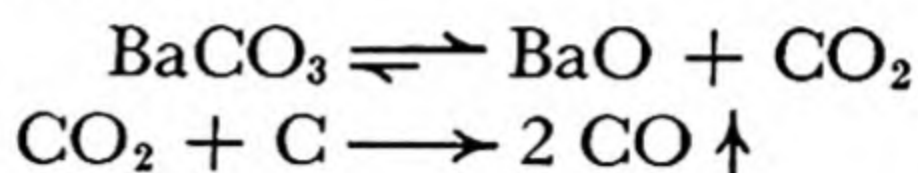
When barium oxide is gently heated with air under pressure, it is converted into the peroxide.

$$2\,BaO + O_2 \rightleftharpoons 2\,BaO_2$$
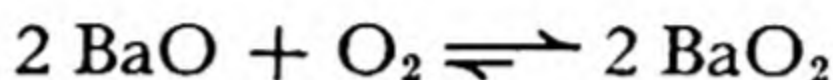
This compound is important as a source of hydrogen peroxide.

Barium hydroxide, $Ba(OH)_2$, is prepared by the hydration of the oxide.

$$BaO + H_2O \longrightarrow Ba(OH)_2$$
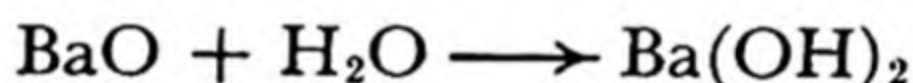
This hydroxide is more stable toward heat than either calcium hydroxide or strontium hydroxide. It may be melted without decomposition at 780°. It is used to a limited extent in sugar refining and as a laboratory reagent.

The Chlorides. *Magnesium chloride*, $MgCl_2$, occurs in sea water and in salt deposits and salt well brines. It may be prepared by the reaction of hydrochloric acid with the oxide, hydroxide, and carbonate. The salt hydrolyzes in hot water, forming magnesium hydroxy ions and hydrogen ions. Consequently, water containing this salt is not suitable for use in steam boilers, because of the corrosion and scale formation which it causes. Magnesium chloride combines with magnesium oxide to form the stable oxychloride, Mg_2OCl_2, *Sorel cement*, which is used in making a smooth surface floor. It is now used to some extent for flooring in munition works and in hospital operating rooms. A grounded grid of copper wire may be embedded in the cement, and the material has sufficient electrical conductivity to allow static charges to be carried off, thus preventing electric sparks.

Calcium chloride, $CaCl_2$, may be prepared by a number of reactions, but is obtained primarily as a by-product of the recovery of ammonia in the Solvay process for soda. (See page 423.) The most important uses of calcium chloride depend on its high solubility in water, 59.5 g. of the anhydrous salt in 100 g. of water at 0°.

The freezing point of water from the saturated solution is $-55°$, and the cold solution is useful as a refrigerating brine in cold storage plants. The solid is deliquescent, absorbing enough water to make it useful in keeping down dust on dirt roads. There are several hydrates of calcium chloride. The anhydrous salt and the dihydrate are used extensively as drying agents.

Barium chloride, $BaCl_2$, and *strontium chloride*, $SrCl_2$, are important laboratory reagents for supplying these metal ions. They may be prepared from the natural sulfates by reduction with carbon to form the sulfides, which react with hydrochloric acid to form the chlorides.

$$BaSO_4 + 4\,C \longrightarrow BaS + 4\,CO$$
$$BaS + 2\,H^+ \longrightarrow Ba^{++} + H_2S \uparrow$$
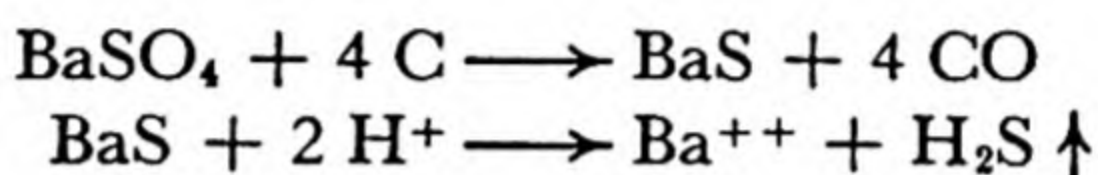
The Sulfates. *Magnesium sulfate*, $MgSO_4$, occurs in salt deposits as *kieserite*, $MgSO_4H_2O$, and *epsomite*, $MgSO_4(H_2O)_7$. It also occurs in mineral waters as in the spring waters at Epsom in England. The salt crystallizes from solution as the heptahydrate at temperatures between 1.8° and 48°. Magnesium sulfate is used in weighting and sizing cotton and silk, in dyeing, in fireproofing fabrics, and in medicine as a purgative. Zinc and ferrous ions also yield sulfates which crystallize as heptahydrates. These salts are similar to magnesium sulfate in crystalline structure and in chemical properties. They decompose when they are heated strongly, water and sulfuric acid, *oil of vitriol*, being distilled from the salt. These salts are often called *vitriols*. The residue from the distillation is a mixture of oxides and oxysulfates.

Calcium sulfate, $CaSO_4$, occurs in nature in two forms, *anhydrite* and *gypsum*. The hydrated salt, *gypsum*, $CaSO_4(H_2O)_2$, is the solid phase in equilibrium with the saturated solution at temperatures below 63.5°; the anhydrous salt, at higher temperatures. The solubility of the salt decreases rapidly with rise in temperature, causing the deposition of boiler scale when water containing this salt is used in steam boilers.

Gypsum is partially dehydrated when it is heated at 125°.

$$2\,CaSO_4(H_2O)_2 \longrightarrow (CaSO_4)_2H_2O + 3\,H_2O$$
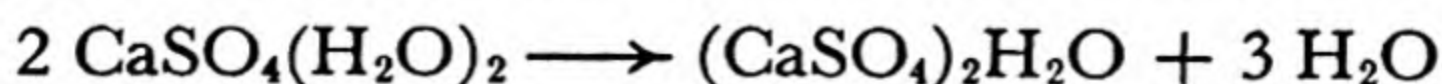
The partially dehydrated product rapidly becomes hydrated again when it is moistened, and it sets to form a crystalline mass. Plaster

of Paris is used in making surgical bandages and different kinds of plaster casts. The most general use is in the making of plaster for the interior of buildings, size or glue being added to retard the rate of setting. Calcium sulfate is used in large quantities in the manufacture of stucco and wallboard, and in Portland cement.

One of the forms of anhydrous calcium sulfate absorbs water so readily that only a very low pressure of water vapor may remain in equilibrium with the solid. This substance, under the trade name Drierite, is used as a drying agent for gases and liquids.

Barium sulfate, $BaSO_4$, and *strontium sulfate*, $SrSO_4$, occur in nature and are the important source materials from which the other compounds are prepared. Since they are the slightly soluble salts of a strong, stable acid, they are not decomposed by the other common acids to produce different barium and strontium salts. Soluble salts may be prepared by first reducing the sulfate to the sulfide, a salt of a weak, volatile acid.

$$SrSO_4 + 4\ C \longrightarrow SrS + 4\ CO \uparrow$$
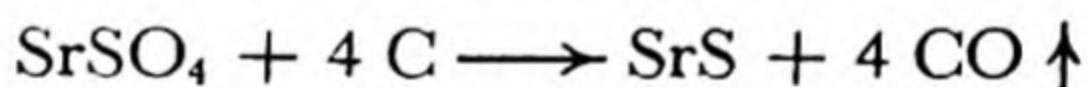
Barium and strontium sulfates are precipitated by the reaction of any soluble sulfate with solutions of barium and strontium salts. The reaction of barium sulfide with a solution of zinc sulfate yields a mixture of the slightly soluble barium sulfate and zinc sulfide.

$$Zn^{++} + SO_4^{--} + BaS \longrightarrow ZnS + BaSO_4$$
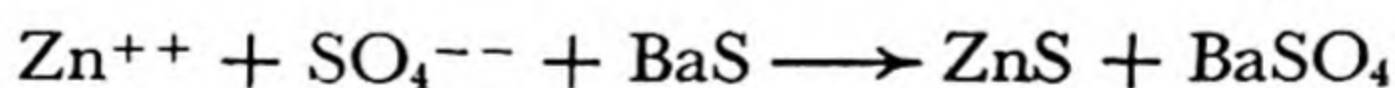
This mixture, known as *lithopone*, is used as a white body in paint, since it does not darken in air containing hydrogen sulfide, as lead white does.

The Carbonates. *Calcium carbonate*, $CaCO_3$. The shells of crustacea are composed largely of this substance. Thick deposits have been formed in past ages; and subsequent metamorphosis has led to the formation of marble, containing only small percentages of impurities, and limestone containing larger proportions of other materials. Calcium carbonate is dimorphous, *i.e.*, it exists in two crystalline forms. Rhombohedral crystals of *calcite* separate from solution at temperatures below 30°, rhombic crystals of *aragonite*, at higher temperatures. Although calcite is the stable form at temperatures below 30°, the rate of transition is slow.

Calcium carbonate exhibits the general reactions of the carbon-

ates. Carbon dioxide is evolved when it reacts with an excess of strong acids, but the hydrocarbonate is formed with low concentrations of hydrogen ions, as in water containing dissolved carbon dioxide.

$$CaCO_3 + 2\,H^+ \longrightarrow Ca^{++} + H_2O + CO_2 \uparrow$$
$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{++} + 2\,HCO_3^-$$
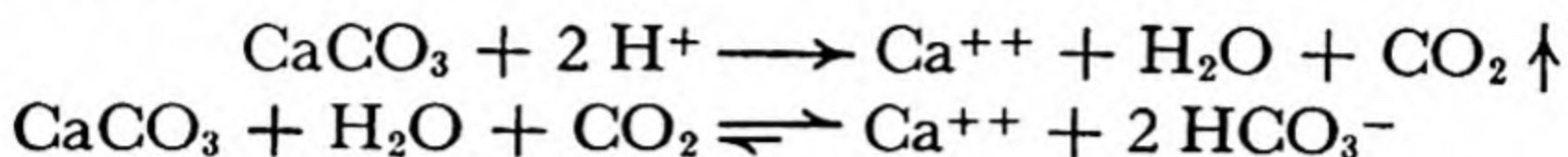
Calcium carbonate is decomposed into calcium oxide and carbon dioxide when heated to temperatures of 700–1000°. It also reacts with acidic oxides, such as silica, when the solids are heated together.

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$
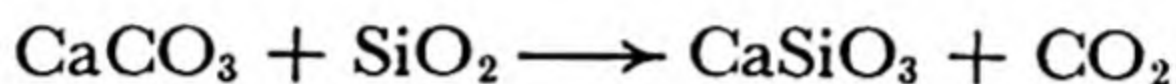
Limestone is used in large quantities in the production of quicklime and cement, as a source of carbon dioxide, in the manufacture of glass, as a flux in the metallurgical processes, and for many other purposes in chemical industry. Limestone and marble are used extensively as building stone and for monuments.

Magnesium carbonate, **MgCO₃**, is easily decomposed by heat to form the oxide. Magnesite and dolomite are extensively used in the steel industry for the construction of furnace linings in the open-hearth process. The reaction of a solution of sodium carbonate with a soluble magnesium salt leads to the precipitation of the hydroxycarbonate, $Mg_4(OH)_2(CO_3)_3$, commonly called a basic carbonate.

$$4\,Mg^{++} + 4\,CO_3^{--} + H_2O \longrightarrow Mg_4(OH)_2(CO_3)_3 + CO_2 \uparrow$$

This compound has medicinal uses under the name, *milk of magnesia*. It is also used in the preparation of tooth paste and powder and in silver polish. A very porous product used as a heat insulator is produced by preparing a mixture of this substance with asbestos.

Bicarbonates. The formation of calcium bicarbonate by the reaction of water and carbon dioxide with calcium carbonate causes the gradual leaching out of limestone. Caves are formed by this action, *e.g.*, Mammoth Cave in Kentucky and the numerous caves in Virginia and other limestone regions. Sink holes result if no roof is supported. The insoluble carbonate is formed when carbon dioxide escapes from solutions of the bicarbonate. This leads to the formation of stalactites and stalagmites in caves. The

bicarbonates of ferrous ions and of magnesium ions are formed in a similar manner. These compounds occur in natural water in some regions. Bicarbonates are converted into normal carbonates by reaction with basic substances and by thermal decomposition.

Hard Water. Water in wells, streams, and lakes usually contains dissolved salts in varying proportions. For many uses, magnesium and calcium salts are especially objectionable in water. Bicarbonates of these metals cause temporary hardness, and the chlorides and sulfates cause permanent hardness.

Hard water has objectionable properties for household and laundry uses because calcium and magnesium ions react with soap. The familiar soaps are sodium or potassium salts of certain organic acids, *e.g.*, sodium stearate, $NaC_{18}H_{35}O_2$. The precipitation of the calcium and magnesium salts of these acids causes a great waste of soap, and the precipitates adhere to fabrics and cause stains.

$$Ca^{++} + 2\,NaC_{18}H_{35}O_2 \rightleftharpoons Ca(C_{18}H_{35}O_2)_2 \downarrow + 2\,Na^+$$
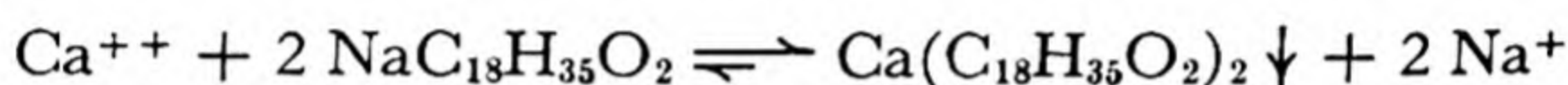
Hard water is unsatisfactory for use in steam boilers, because of the formation of boiler scale. The deposits collect in dense layers inside of the boiler tubes. They are poor conductors of heat, and their presence makes high temperatures necessary to maintain the required steam pressure. This not only causes a great waste of fuel but also increases the rate of corrosion of the boiler tubes, by air outside and by water inside of the boiler. Magnesium chloride in boiler water is especially harmful because the hydrated magnesium ion is acidic. It hydrolyzes at high temperatures to form hydrogen ions in sufficient concentration to cause corrosion of the metal of which the boiler is constructed.

Water softening is accomplished by treating hard water with the proper precipitating agents. Insoluble compounds are removed by allowing them to settle or by filtration. Bicarbonates are easily removed by the addition of the correct quantity of slaked lime to convert them into normal carbonates.

$$Ca^{++} + HCO_3^- + OH^- \rightleftharpoons CaCO_3 \downarrow + H_2O$$
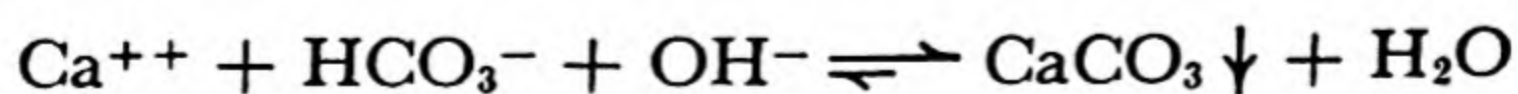
Other magnesium salts may be removed by precipitating the hydroxide. Lime too is used for this purpose, but this introduces an equivalent quantity of calcium ions, which are also objectionable.

Therefore, the calculated quantity of sodium carbonate is added along with the lime to cause the precipitation of calcium carbonate in addition to magnesium hydroxide.

$$Mg^{++} + 2\,OH^- \rightleftharpoons Mg(OH)_2 \downarrow$$
$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3 \downarrow$$
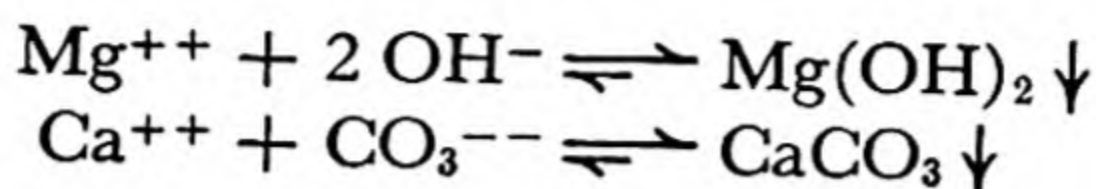
Sodium phosphate is also used in softening hard water. The phosphate ion is basic enough to neutralize acidic materials, and it also causes the precipitation of the phosphates of calcium and magnesium. Borax is used for water softening in household practice. The sodium salts produced during the softening do not have the objectionable properties shown by the magnesium and calcium compounds.

EXERCISES

1. Which compounds of the metals of the alkaline earth group are commonly used as source materials of the metals and their other compounds?
2. What method is usually employed for the production of the alkaline earth metals? Why is this the method selected?
3. Indicate the steps involved in the preparation of the fused electrolyte for the production of metallic magnesium from (a) salt well brines, (b) sea water, and (c) magnesium carbonate or magnesium oxide.
4. What steps are necessary for the production of metallic magnesium from the oxide by reduction with carbon?
5. Describe the production of metallic magnesium in the process employing silicon as the reducing agent. What special factors cause the success of this process?
6. Represent by equations reactions characteristic of these metals.
7. What general method is used for the production of the oxides of the alkaline earth metals?
8. How are the anhydrous chlorides of magnesium and beryllium prepared? Why can they not be satisfactorily prepared by the direct dehydration of the hydrates by heat?
9. How can soluble salts of barium and strontium be prepared from the sulfates of these metals? Explain.
10. Explain the solution of calcium carbonate in water containing dissolved carbon dioxide.
11. What is meant by hard water? Into what two groups may the objectionable materials in hard water be classified?
12. What objectionable properties are shown by hard water if used in laundry or as boiler feed water?
13. Discuss the removal of materials causing hardness of water and illustrate the reactions by equations.

SUPPLEMENTARY READINGS

Weeks, M. E., *The Discovery of the Elements*, Journal of Chemical Education, Easton, Pa., 1935, chap. X.

Creighton, H. J., and W. A. Koehler, *Electrochemistry*, John Wiley & Sons, Inc., New York, 1935, Vol. II, pp. 238–55.

Kirkpatrick, S. D., "Magnesium by the Hansgirg Process," *Chem. Met. Eng.* **48**, 9, 91 (1941).

Stedman, G. E., "Ford Makes Magnesium," *Chem. Met. Eng.* **49**, 9, 134 (1942).

Ramsey, R. H., "Magnesium — Production at the World's Largest Plant," *Chem. Met. Eng.* **50**, 10, 98 (1943).

"Magnesium from Sea Water," Pictured Flow Sheet, *Chem. Met. Eng.* **48**, 11, 130 (1941).

Silliman, H. F., "Beryllium-Copper Alloys," *Ind. Eng. Chem.* **28**, 1424 (1936).

Sawyer, C. B., and B. R. Kjellgren, "Newer Developments in Beryllium," *Ind. Eng. Chem.* **30**, 501 (1938).

Powell, S. T., and H. E. Bacon, "Industrial Water Supplies," *Ind. Eng. Chem.* **29**, 615 (1937).

Chapter 28

ALUMINUM

Aluminum is the only industrially important metal in Group III of the periodic system. *Boron*, the element of lowest atomic number in this group, is nonmetallic, and the elements of the higher atomic numbers are metallic but not important. Aluminum is the most abundant metal in the outer crust of the earth. Complex silicates containing aluminum are the most abundant of the minerals, *e.g.*, *orthoclase*, $KAlSi_3O_8$, *muscovite*, $KAl_3H_2(SiO_4)_3$, and *kaolinite*, $Al_2Si_2O_7(H_2O)_2$. The only important ore of aluminum at the present time is *bauxite*, composed of the hydrated oxides, $Al_2O_3(H_2O)$ and $Al_2O_3(H_2O)_3$. Approximately 95 per cent of the bauxite ore produced in the United States is obtained from Arkansas, the remainder coming from Alabama and Georgia. Large deposits of this important ore are found in Surinam, British Guiana, France, Hungary, and Yugoslavia. The mineral *cryolite*, Na_3AlF_6, found in Greenland, is used in the production of the metal from bauxite.

The Production of Aluminum. Aluminum was first prepared in 1825 by Oersted by the reduction of the chloride with potassium amalgam. A method for the commercial production of the metal by the reduction of the chloride with sodium was developed by Deville, about 1850. Improvements in the process brought the price down from about $75 a pound in 1856 to $4 a pound in 1886. These prices were too high to permit extensive uses of the metal. The problem of producing aluminum at low cost was solved independently in 1886 by Hall in the United States and by Heroult in France. Both investigators developed the same method in principle, the electrolysis of aluminum oxide dissolved in melted cryolite. The production of aluminum in the United States in 1943 was more than 900,000 tons. The price of aluminum is now 14–15 cents per pound.

Two essential steps are involved in the production of aluminum, *viz.*, the preparation of the relatively pure oxide from the ore and the reduction of the oxide by electrolysis. An outline of the procedure is shown in Fig. 119.

Preparation of the Oxide. Most of the impurities in the bauxite ore are compounds of metals having lower activity than aluminum.
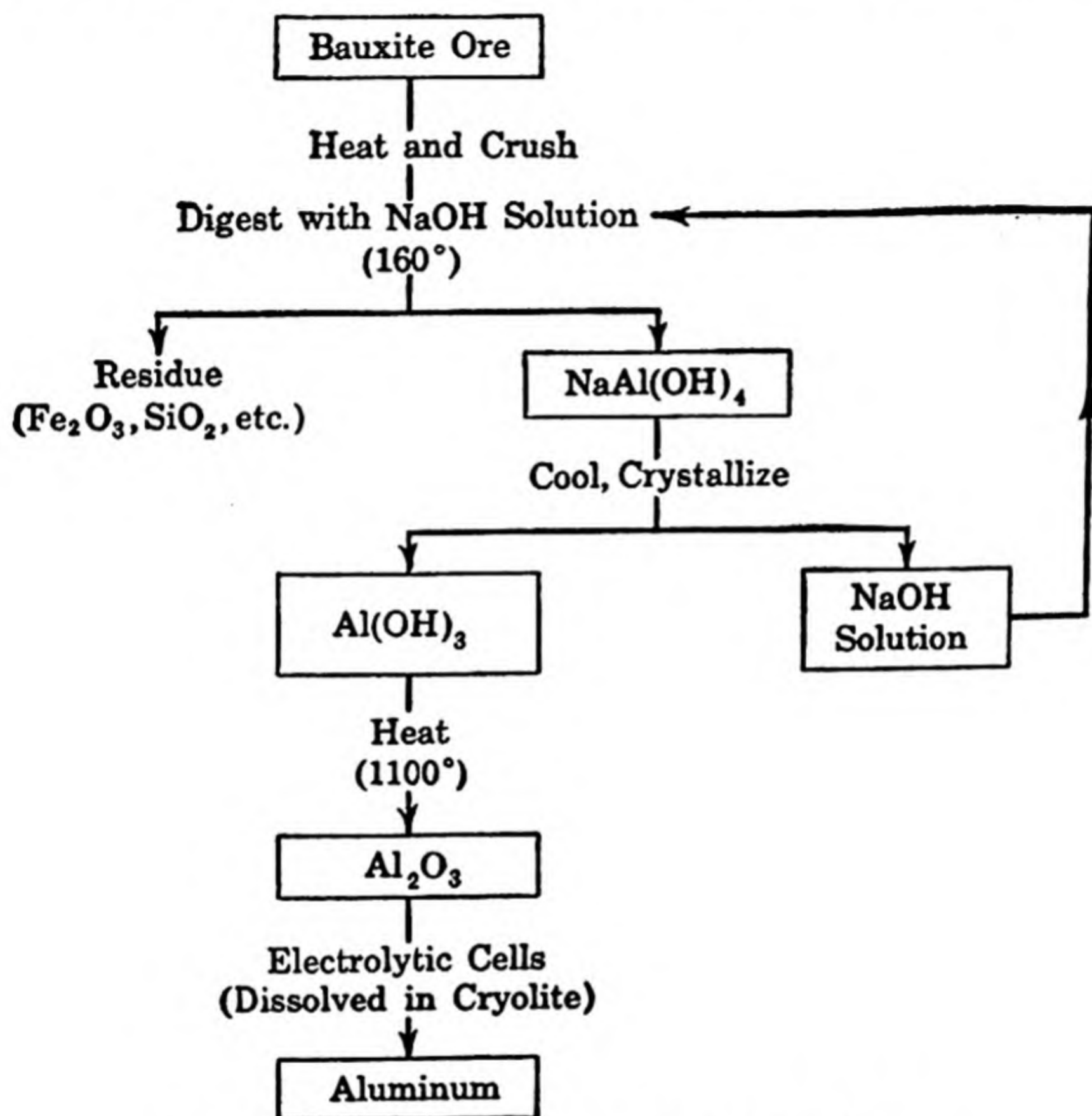
Fig. 119. Outline — Production of Aluminum

If the crude ore were used directly in the electrolytic process, these metals would be liberated along with aluminum, producing an impure product. In order to prepare pure aluminum oxide from ores having low silica content, *e.g.*, bauxite from Surinam, the crude ore is ground to a powder and digested with sodium hydroxide solution heated under pressure to 160–170°. Most of the aluminum oxide is dissolved under these conditions, leaving iron oxide in the residue.

$$Al_2O_3 + 3 H_2O + 2 OH^- \rightleftharpoons 2 Al(OH)_4^-$$
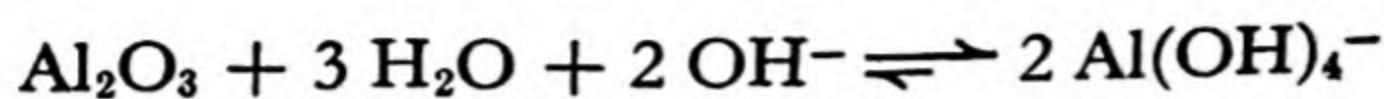
This solution is separated from the residue and aluminum hydroxide, or the hydrated oxide is precipitated by adding some of the crystalline hydroxide to induce crystallization as the solution cools.

$$Al(OH)_4^- \rightleftharpoons Al(OH)_3 \downarrow + OH^-$$
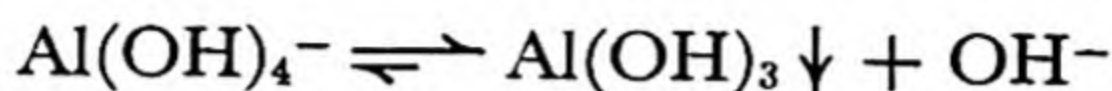
This method recovers only approximately 70 per cent of the oxide from bauxite ores containing large percentages of silica, e.g., the Arkansas ores, about 13 per cent of silica. The residue from the sodium hydroxide treatment is a red mud containing compounds
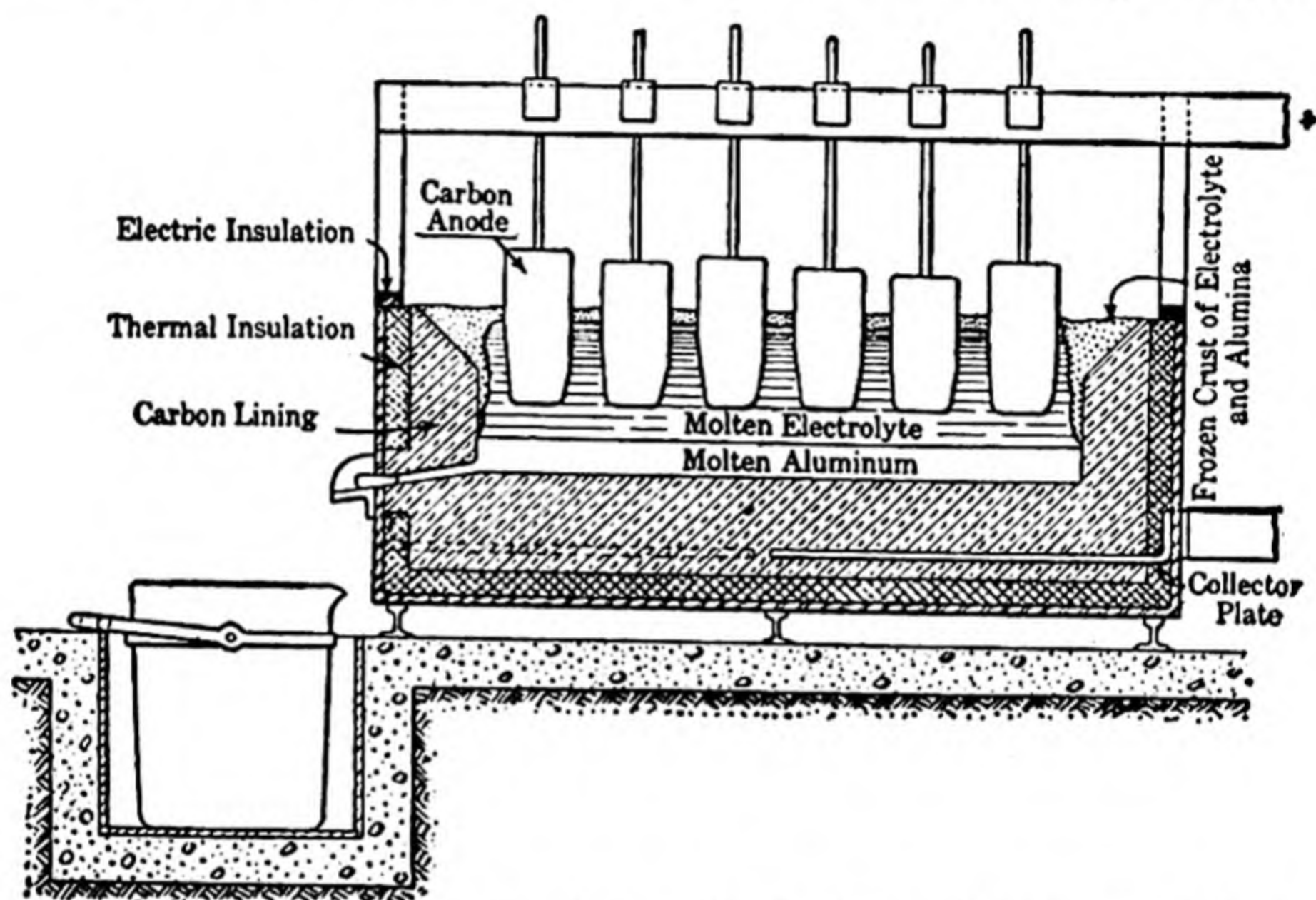
Fig. 120. *Cell for Electrolytic Production of Aluminum. (Courtesy of Aluminum Company of America)*

of iron, titanium, and silicon, with the aluminum compounds. Aluminum oxide may be recovered from this mud by mixing the dried material with limestone and soda, and heating the mixture until it begins to fuse. The product is extracted with water, and the solution is used to leach the oxide from the crude bauxite ore. The precipitated hydroxide is heated to form the anhydrous oxide which has a purity of approximately 99.5 per cent when prepared by this method. Methods have been developed for the preparation of the oxide from some of the complex aluminum silicates, but these methods have not yet come into extensive commercial use.

The Electroformation of Aluminum. The electrolytic reduction

of aluminum oxide by the Hall process is carried out in strong steel cells (Fig. 120) lined with a relatively thick layer of carbon, prepared by baking a mixture of coke and tar in position on the inner surface of the cell walls. The anodes are large carbon rods that extend down into the cell. In order to begin the operation of a cell, the anodes are lowered until an arc is formed between the anodes and the carbon lining of the cell. Cryolite or the synthetic sodium aluminofluoride is introduced and is melted by the heat of the arc. Purified aluminum oxide is then added and the anodes
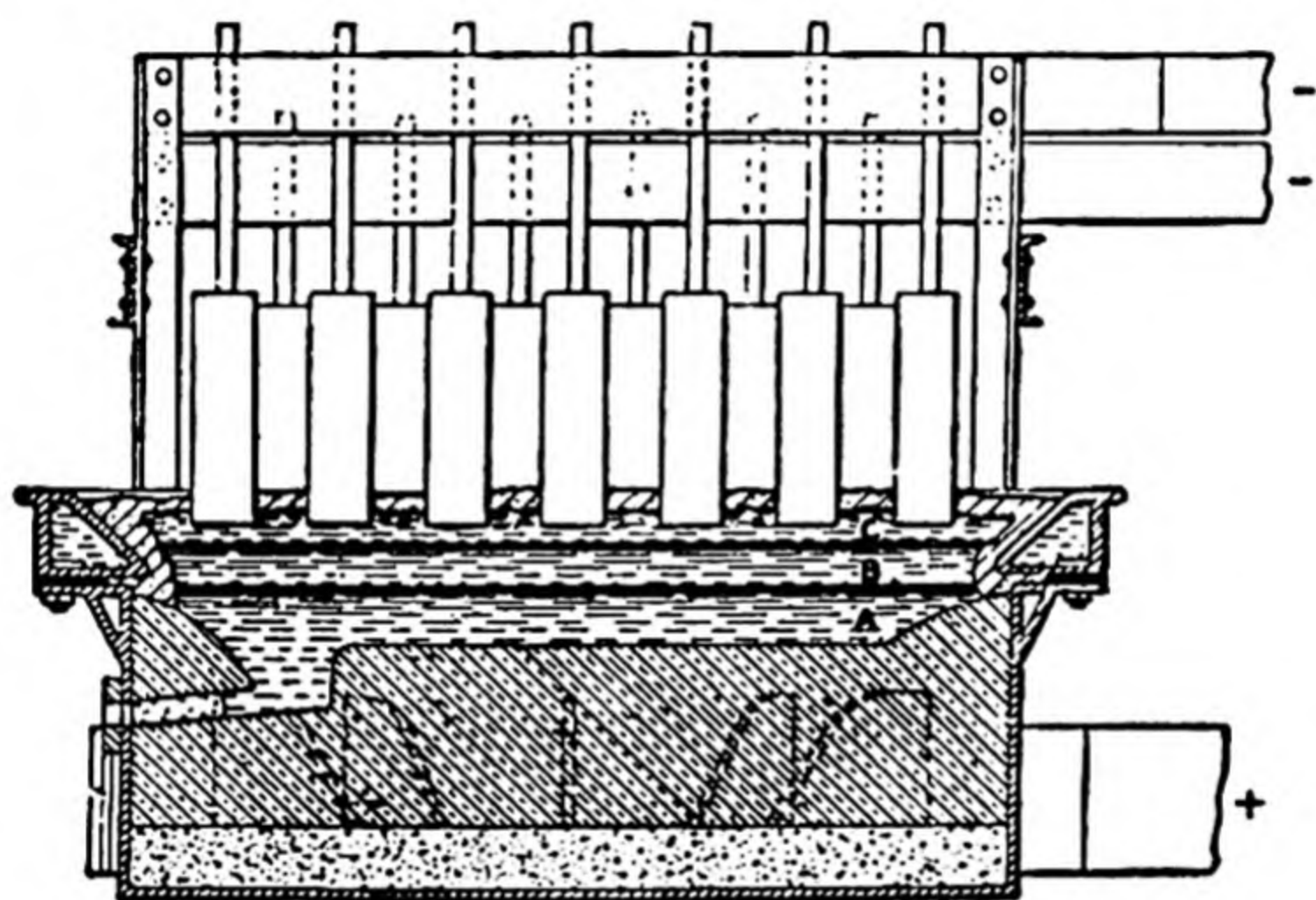
Fig. 121. Cell for the Electro-Refining of Aluminum

are raised and adjusted at the proper height to cause the current to flow through the solution of the oxide in the fluoride. The temperature is maintained at approximately 1000° by the resistance of the electrolyte to the passage of the current. The voltage drop per cell is about 6 volts. Forty to one hundred cells are connected in series, and the amperage for each line of cells is from 10,000 to 30,000 amperes.

Aluminum is discharged at the cathode and collects at the bottom of the cell, since it is more dense than the electrolyte. From time to time, the molten metal is drawn off and cast into bars and ingots. Oxygen is discharged by reaction with carbon at the anode to form carbon monoxide or carbon dioxide. The anodes are gradually used up by the reaction and must be replaced. The oxide is introduced at suitable intervals without interrupting the process. The purity of the product is 99–99.5 per cent. The product may be

refined for uses that require the metal in a higher degree of purity.

The Electrorefining of Aluminum. The refining of aluminum may be carried out by an electrolytic process. Anhydrous electrolytes must be employed as in the production of the metal. Aluminum is molten at the temperatures required to melt the electrolyte. Hence, the electrolytic cell must provide for three liquid layers, the anode, the electrolyte, and the cathode, all at high temperature. *In the Hoopes process* (Fig. 121) the lower layer A, the anode, is an alloy of aluminum, copper, and silicon of such density that it remains in a separate layer. The middle layer B, the electrolyte, is a fused salt mixture of the fluorides of sodium, aluminum, and barium, nearly saturated with aluminum oxide. The upper layer C, the cathode, is the pure metal. The composition of the electrolyte must be such as to give it a density greater than the pure metal, but less than the alloy used as the anode.

The passage of the current causes the discharge of aluminum ions from the electrolyte at the cathode.

$$Al^{+++} + 3\,\epsilon \longrightarrow Al$$
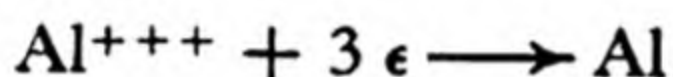
An equivalent quantity of aluminum goes into solution at the anode.

$$Al \longrightarrow Al^{+++} + 3\,\epsilon$$
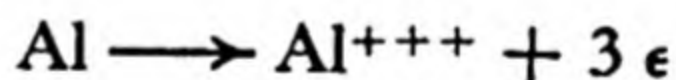
Other cations in the electrolyte are ions of metals more active than aluminum. Therefore, they do not deposit at the cathode. Other metals in the anode are less active than aluminum. Hence, they do not dissolve at the anode. Aluminum is transported from the anode to the cathode through the intermediate formation of ions.

Properties of Aluminum. The metal has low density, 2.7 g. per milliliter at 20°, and a low melting point, 658.7°. Its normal boiling point is 1800°. The metal is malleable and ductile and may be given relatively high tensile strength by cold working such as rolling. Aluminum is a good conductor of heat and electricity. In wires of equal size, copper is the better conductor of electricity, but in wires of equal weight per lineal foot, aluminum is about twice as good a conductor as copper.

Reactions of Aluminum. The atoms of aluminum contain three valence electrons, and they release electrons actively to form elec-

trovalent ions with an oxidation number of 3+. The surface of metallic aluminum becomes coated with an adherent film of the oxide which protects the metal from atmospheric oxidation and from reaction with water. The amalgamated metal reacts readily with oxygen and with water, because the oxide coating does not adhere to the amalgamated surface.

$$4\ Al + 3\ O_2 \longrightarrow 2\ Al_2O_3$$
$$2\ Al + 6\ H_2O \longrightarrow 2\ Al(OH)_3 + 3\ H_2$$
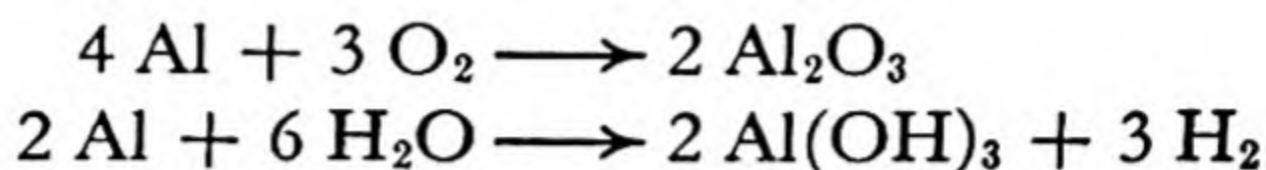
Aluminum reacts with water containing sodium hydroxide or sodium carbonate, because the oxide coating is dissolved by the basic solution.

$$2\ Al + 6\ H_2O + 2\ OH^- \longrightarrow 2\ Al(OH)_4^- + 3\ H_2$$
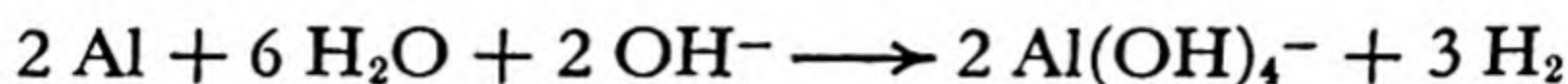
Aluminum reacts vigorously with the halogens, with sulfur, and with carbon.

$$2\ Al + 3\ S \longrightarrow Al_2S_3$$
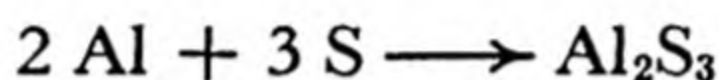
It also reacts readily with dilute sulfuric acid and with hydrochloric acid.

$$2\ Al + 6\ H^+ \longrightarrow 2\ Al^{+++} + 3\ H_2$$
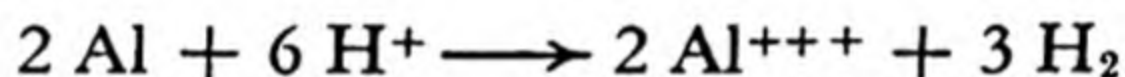
Aluminum becomes "passive" in contact with nitric acid, so that it does not ordinarily react with this acid. The passivity of the metal is usually attributed to the formation of a surface film of the oxide. At high temperatures, aluminum reacts with the oxides of a number of the metals to form the uncombined metal and aluminum oxide.

$$4\ Al + 3\ MnO_2 \longrightarrow 2\ Al_2O_3 + 3\ Mn$$
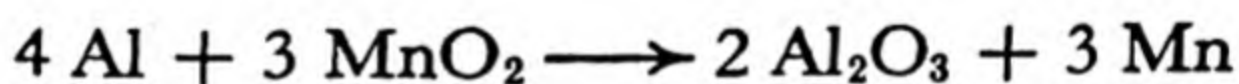
Uses of Aluminum. Consideration of the properties of aluminum indicates its suitability for many uses. An important use is in the production of alloys having the desirable properties of lightness and strength. The principal alloying elements used with aluminum are copper, silicon, manganese, magnesium, and zinc. The properties of the alloys vary greatly depending on the proportions of these elements. *Duralumin*, the strongest of the aluminum alloys, contains about 94 per cent of aluminum, 4 per cent of copper, 0.5 per cent of magnesium, 0.5 per cent of manganese, with smaller percentages of silicon and iron. This alloy is extensively used in

the construction of airplanes, motor trucks and busses, and in other fields of transportation. Duralumin may be coated with a thin layer of pure aluminum to protect it from corrosion. This product is marketed as Alclad sheet. Aluminum alloys may also be protected from corrosion by the formation of the oxide protective coating in an electrolytic process. The object is made the anode in an electrolyte consisting of dilute sulfuric acid, boric acid, and chromic acid.

Other important uses of aluminum, restricted now because of the large requirements for aluminum in aircraft construction, are in the manufacture of cooking utensils and household appliances, of cables for long distance transmission of electricity, of foil for protective wrapping, of powdery flakes mixed with varnish or a lacquer for paint, and for many other purposes.

Aluminum is used in the steel industry to combine with oxygen which otherwise would cause flaws and weaken steel. The production of certain metals from their oxide ores in the process called *aluminothermy* employs aluminum as an active reducing agent. An important example of this is in thermit welding. Thermit, a mixture of aluminum and an oxide of iron, is placed in a clay crucible and ignited by means of an ignition powder consisting of barium peroxide and magnesium powder. A violent reaction follows, and the iron oxide is reduced, liberating the metal which sinks to the bottom of the crucible.

$$3 \, Fe_3O_4 + 8 \, Al \longrightarrow 4 \, Al_2O_3 + 9 \, Fe$$
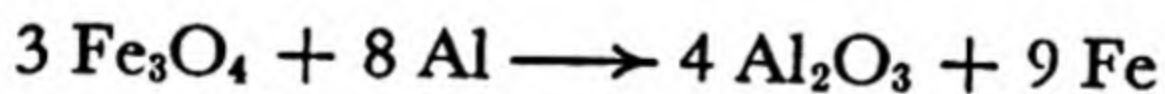
The melted iron is allowed to flow from the crucible into a sand mold around the cleaned and preheated ends of the metal to be welded. Repairs to heavy machinery may be made in this way without the necessity of dismantling the machine.

The thermit mixture is also used in incendiary bombs. Mixtures of aluminum powder or flakes with perchlorates or nitrates and a binder, such as shellac, are used as aluminum flares in aviation for signaling and for illuminating landing fields and military objectives.

The Oxide and Hydroxide of Aluminum. Aluminum oxide occurs naturally in several forms. *Corundum* and *emery* that contains also some magnetite are hard substances used as abrasives. *Alundum*, an artificial corundum, is prepared by melting the oxide in an

electric furnace. It is also used as an abrasive and as a refractory material. The *ruby* is a crystalline form of the oxide, colored by a trace of chromium, and the *sapphire* is colored by the presence of iron and titanium. Synthetic gems, which are chemically identical with those found in nature, are produced by fusing the oxide and allowing it to crystallize under the proper conditions. In addition to its use as the ore of aluminum metal, bauxite has a number of important uses, *e.g.*, in the manufacture of abrasives, in the production of aluminum compounds, in oil refining, and in the production of refractory materials.

A gelatinous precipitate, commonly called *aluminum hydroxide*, is formed by the reaction of aluminum ions with low concentrations of hydroxide ions. This substance is usually represented by the formula $Al(OH)_3$, although the more nearly complete formula is $Al(H_2O)_3(OH)_3$. Salts of weak acids, such as the soluble carbonates and sulfides, contain anion bases sufficiently active to cause the precipitation of aluminum hydroxide.

$$2 Al(H_2O)_6^{+++} + 3CO_3^{--} \longrightarrow 2Al(H_2O)_3(OH)_3 \downarrow + 3CO_2 + 3H_2O$$
$$2 Al(H_2O)_6^{+++} + 3 S^{--} \longrightarrow 2 Al(H_2O)_3(OH)_3 \downarrow + 3 H_2S$$
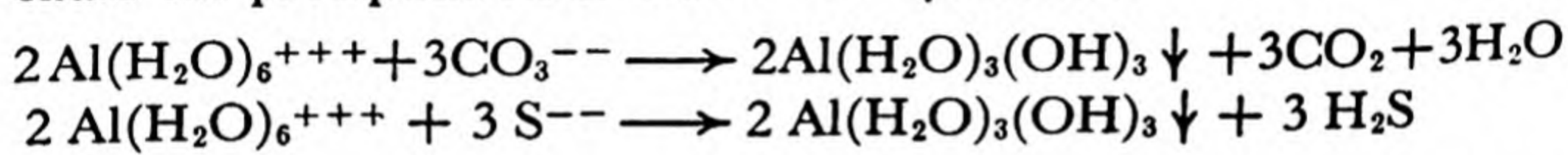
The molecules of water of hydration may be omitted from these formulas to give the simplified equations:

$$2 Al^{+++} + 3 CO_3^{--} + 3 H_2O \longrightarrow 2 Al(OH)_3 \downarrow + 3 CO_2$$
$$2 Al^{+++} + 3 S^{--} + 3 H_2O \longrightarrow 2 Al(OH)_3 \downarrow + 3 H_2S$$
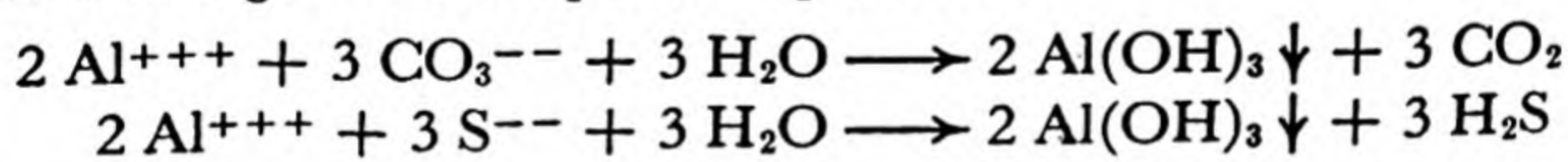
Aluminum hydroxide is amphoteric, reacting as both an acid and a base, *i.e.*, giving up protons to stronger bases and taking on protons from stronger acids.

$$Al(H_2O)_3(OH)_3 + OH^- \rightleftharpoons Al(H_2O)_2(OH)_4^- + H_2O$$
$$Al(H_2O)_3(OH)_3 + 3 H^+ \rightleftharpoons Al(H_2O)_6^{+++}$$
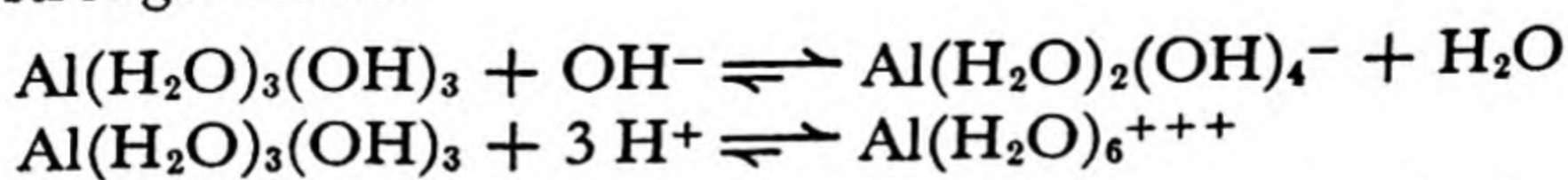
A porous form of alumina is produced by heating the hydroxide.

$$2 Al(OH)_3 \longrightarrow Al_2O_3 + 3 H_2O$$
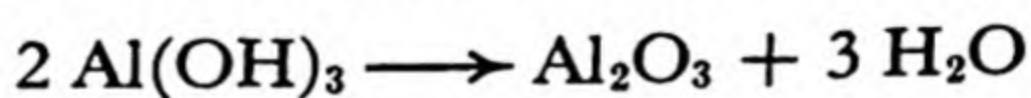
This product absorbs water so readily that it is a good dehydrating agent.

Salts of Aluminum. The metal yields two series of salts, *viz.*, salts containing hydrated aluminum ions, $Al(H_2O)_6^{+++}$, commonly written Al^{+++}, and salts containing the aluminate ions,

$Al(H_2O)_2(OH)_4^-$, commonly written $Al(OH)_4^-$ or AlO_2^-. The most important aluminum salts are the chloride and sulfate. Solutions of these salts are acidic because they contain a cation acid.

$$Al(H_2O)_6^{+++} + H_2O \rightleftharpoons Al(H_2O)_5OH^{++} + H_3O^+$$
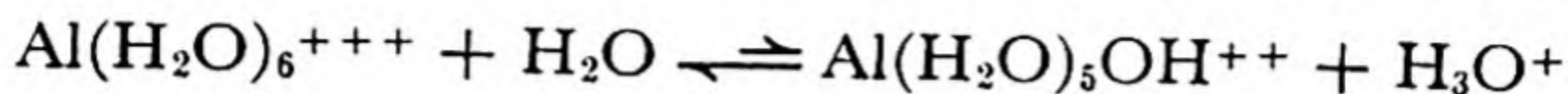
Aluminum chloride, **AlCl₃,** may be prepared in solution by the reaction of hydrochloric acid with the metal or the hydroxide.

$$2\,Al + 6\,H^+ \longrightarrow 2\,Al^{+++} + 3\,H_2$$
$$Al(OH)_3 + 3\,H^+ \longrightarrow Al^{+++} + 3\,H_2O$$
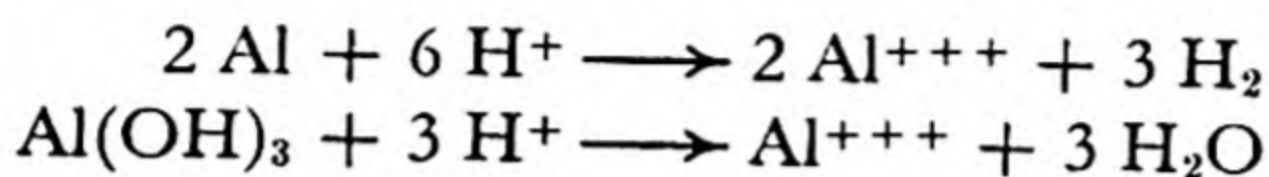
The hydrated salt, $AlCl_3(H_2O)_6$, crystallizes when the solution is concentrated. The evaporation of the solution to dryness, followed by heating the residue, produces the oxide.

$$2\,AlCl_3(H_2O)_6 \longrightarrow Al_2O_3 + 6\,HCl \uparrow + 9\,H_2O \uparrow$$
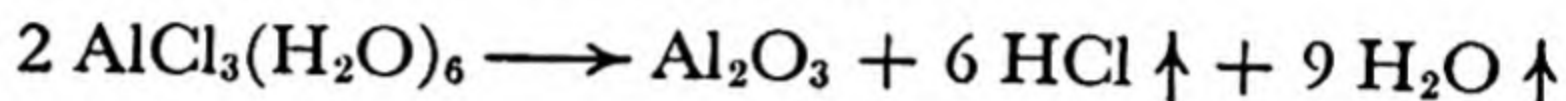
The anhydrous chloride is an important catalyst in a number of reactions in organic chemistry. It is commonly prepared by heating a mixture of aluminum oxide and coke in an atmosphere of chlorine at a temperature of approximately 1000°.

$$Al_2O_3 + 3\,C + 3\,Cl_2 \longrightarrow Al_2Cl_6 + 3\,CO$$
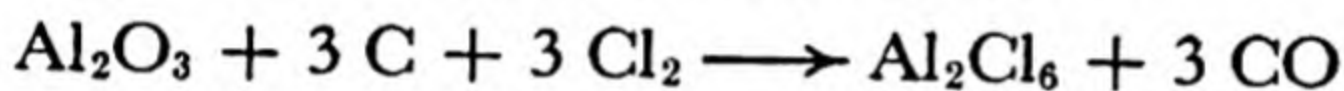
The solid sublimes without melting, and molecular weight determinations indicate the formula of the gas to be Al_2Cl_6.

Aluminum Sulfate, **Al₂(SO₄)₃.** Aluminum sulfate is one of the most important of the aluminum salts. It is prepared by the reaction of the oxide with sulfuric acid.

$$Al_2O_3 + 6\,H^+ \longrightarrow 2\,Al^{+++} + 3\,H_2O$$
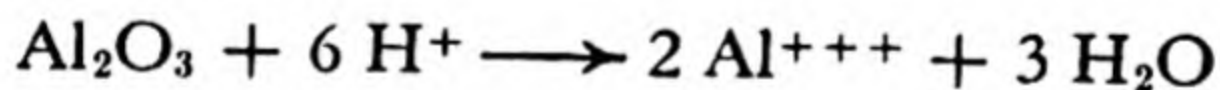
The hydrate, $Al_2(SO_4)_3(H_2O)_{18}$, may be crystallized from solutions of aluminum sulfate. This salt is soluble enough to melt in its own water of hydration when it is warmed. Its solutions are acidic on account of hydrolysis.

When solutions containing equimolar amounts of aluminum sulfate and potassium sulfate are evaporated to the point of crystallization, octahedral crystals of the double salt, *potassium alum,* $KAl(SO_4)_2(H_2O)_{12}$, separate as the solution is allowed spontaneously to evaporate further. With the exception of lithium, the ions of the alkali metals and the ammonium, silver, and thallous ions form isomorphous compounds of the same type. Other trivalent

ions, such as the ferric, chromic, and titanic ions, may replace aluminum ions in these crystals, forming a class of products known as *alums*. The alums may be purified by crystallization, because they are much more soluble in hot water than in cold water. Alums are used in sizing paper and in fireproofing cloth, but the most important uses of aluminum sulfate and aluminum alums depend on hydrolysis of aluminum ions to form acidic solutions and on precipitation of gelatinous aluminum hydroxide.

$$Al(H_2O)_6^{+++} + H_2O \rightleftharpoons Al(OH)(H_2O)_5^{++} + H_3O^+$$
$$Al(H_2O)_6^{+++} + 3\ OH^- \rightleftharpoons Al(OH)_3(H_2O)_3 \downarrow + 3\ H_2O$$
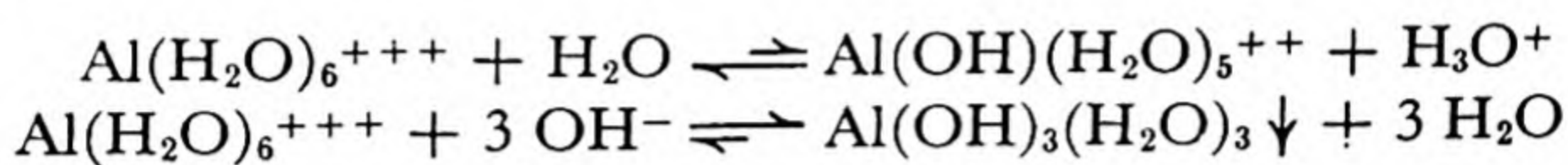
The use of alum in baking powder is due to reaction with bicarbonate ions to form carbon dioxide. This reaction is also applied in some fire extinguishers, in which the acidic alum solution reacts with a bicarbonate solution containing organic substances that aid in the formation of a foam containing carbon dioxide. This blankets the fire, cutting off the oxygen needed for continued combustion. The reaction of sodium carbonate solution or of lime with an alum solution produces a precipitate of hydrated alumina, which adsorbs suspended matter as it settles and aids in the clarification of water. Certain dyes may also be adsorbed by hydrated alumina to produce pigment "lakes." The precipitate is filtered, dried, and ground in oil to prepare pigments for oil paints. Alums are used in mordanting cotton goods. The aluminum hydroxide formed and adsorbed by the fiber of the cloth adsorbs the dye.

EXERCISES

1. What is the important ore of aluminum, and where is it found in useful deposits?
2. What general method is employed for the production of metallic aluminum? Why is this method used?
3. Describe the preparation of aluminum oxide for use in this process, and indicate how the purification of the oxide is accomplished.
4. Describe the Hall process for the production of aluminum.
5. Describe the process for the electrorefining of aluminum, giving reasons for each of the steps employed.
6. Discuss the uses of aluminum, indicating the property or properties which contribute to its usefulness for each of these purposes.
7. Explain the acidity of solutions of aluminum sulfate and aluminum chloride.
8. How is anhydrous aluminum chloride prepared? Why is it important?

SUPPLEMENTARY READINGS

Weeks, M. E., *The Discovery of the Elements*, Journal of Chemical Education, Easton, Pa., 1935.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chap. 18.

Holmes, H. N., "The Story of Aluminum," *J. Chem. Education* 7, 233 (1930).

Deppler, J. H., "Thermit — Its Uses in War and Industry," *Chem. Met. Eng.* 49, 7, 93 (1942).

Lee, J. A., "Three Plants in One," *Chem. Met. Eng.* 50, 5, 145 (1943).

"From Bauxite to Aluminum," Pictured Flow Sheet, *Chem. Met. Eng.* 50, 6, 140 (1943).

Chapter 29

THE METALS OF GROUP IV

Germanium, tin, and *lead* are classified in Group IV of the periodic system with *carbon* and *silicon.* The atoms of these elements contain four valence electrons, but the outer shell of the kernels of the atoms of germanium, tin, and lead contain eighteen electrons instead of eight, as in carbon and silicon. Germanium, tin, and lead yield compounds with the oxidation numbers 2 + and 4 +. In the high oxidation state, the nonmetallic character of the elements predominates, and the compounds are similar to those of silicon. The stability of the compounds in the lower oxidation state increases in the order of the atomic numbers, so that the most important compounds of tin and lead are those in which the metals have an electrovalence of 2 +. The hydroxides of the elements in this state are amphoteric. Some of the properties of the three elements are listed in Table 36.

TABLE 36. PROPERTIES OF GERMANIUM, TIN, AND LEAD

Property	Germanium	Tin	Lead
Atomic weight	72.6	118.7	207.2
Atomic number	32	50	82
Isotopes	70, 72, 73, 74, 76	112, 114, 115, 116, 117, 118, 119, 120, 122, 124	204, 206, 207, 208
Electron structure	2, 8, 18, 4	2, 8, 18, 18, 4	2, 8, 18, 32, 18, 4
Oxidation states	2 +, 4 +	2 +, 4 +	2 +, 4 +
Typical ions	Ge^{++}, GeO_3^{--}	Sn^{++}, $Sn(OH)_4^{--}$ $Sn(OH)_6^{--}$	Pb^{++}, $Pb(OH)_4^{--}$ PbO_3^{--}
Melting point (° C.)	958.0	231.8	327.5
Boiling point (° C.)	2700	2270	1613
Density at 20°, g. per ml.	5.36	7.28	11.34

Germanium. Some of the sulfide ores of silver, lead, and zinc contain germanium. The dioxide is formed by roasting the sulfide, and the metal may be obtained by the reduction of the oxide with

carbon at moderately high temperatures. Germanium is a grayish-white metal, as predicted by Mendeléef before its discovery. It is not important industrially. The most stable compounds of germanium contain the element in the oxidation state 4 +. The dioxide reacts with hydrochloric acid to form the tetrachloride, $GeCl_4$, and with sodium hydroxide to form sodium germanate, Na_2GeO_3. The oxide in the lower state of oxidation, GeO, reacts with acids to form germanous salts and with bases to form germanites. The germanous ion is an active reducing agent.
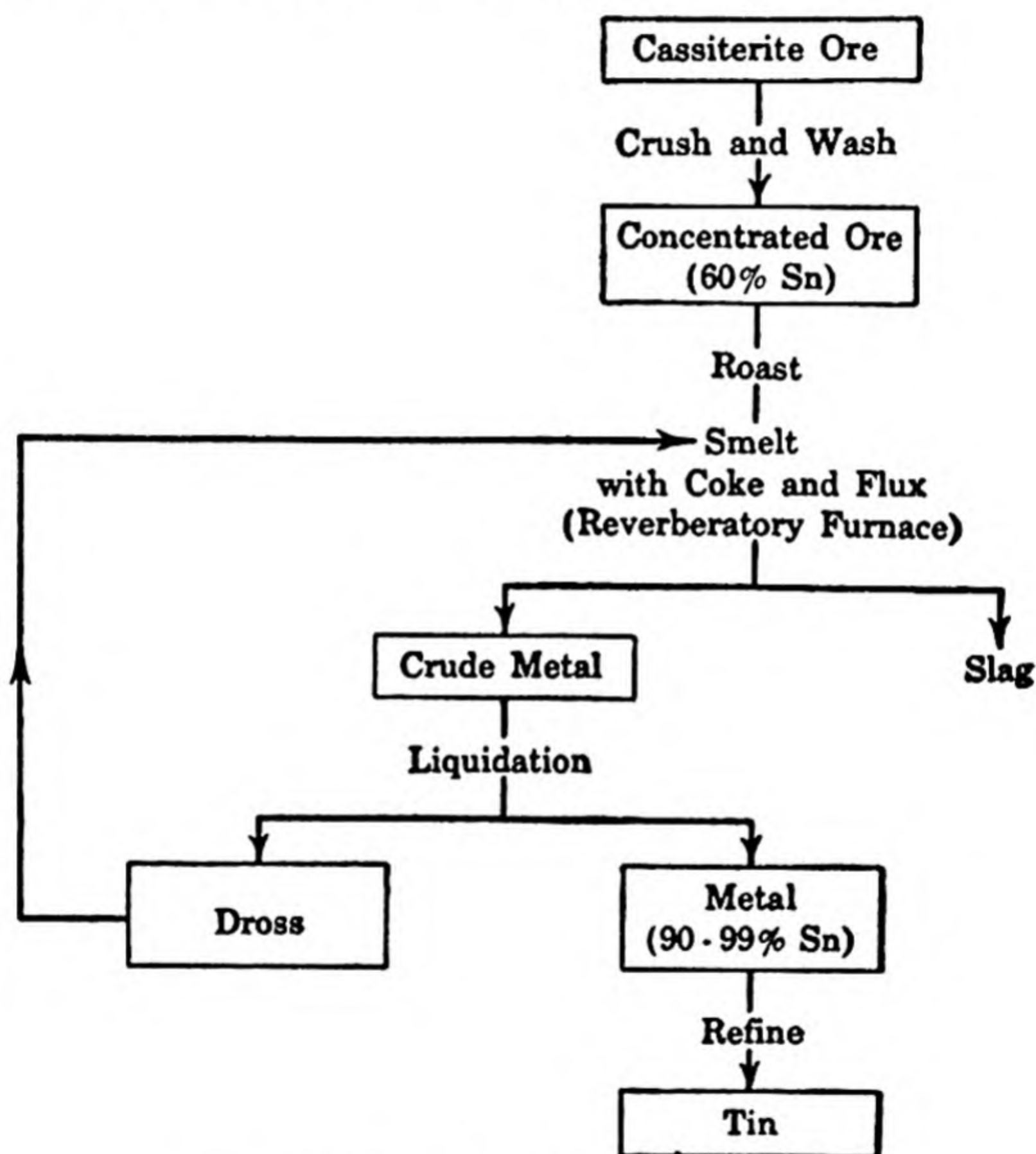
Fig. 122. Outline — Production of Tin

TIN

This metal was known and used by the peoples of ancient times. The Phoenicians secured tin ore from Cornwall in England as early as 1000 B.C. The only important ore of tin is the dioxide, *cassiterite*, SnO_2. The largest deposits of tin ores are in the Malay

States, the Dutch East Indies, and Bolivia. No important deposits of tin ores have been discovered in the United States. It is one of the strategically important metals, since it is needed for the production of tinplate and a number of alloys.

The Production of Tin. The essential steps for the production of metallic tin from the oxide ore are indicated in outline in Fig. 122. The ore is crushed and concentrated by washing. Silicates, less dense than particles of cassiterite, are washed away from the tin ore. The concentrated ore is roasted in air to remove sulfur and arsenic in the form of their volatile oxides. Tin dioxide is next reduced by heating with carbon in a reverberatory furnace.

$$SnO_2 + 2\,C \longrightarrow Sn + 2\,CO$$
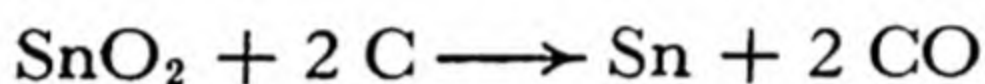
The ores contain silica and, consequently, a basic flux is added to form a slag. Some of the iron oxide in the ore is reduced to metallic iron that alloys with tin, and some of the tin goes into the slag as stannous silicate. The metal and slag are not soluble in each other, and the metal is more dense than the slag. The slag usually contains enough tin to justify further treatment in a second furnace with different fluxes and at higher temperatures.

Usually, the separation of tin from other metals in the crude product is accomplished by *liquation*. This process consists in heating the solid impure metal in a reverberatory furnace with a sloping hearth at a temperature just above the melting point of tin. The pure metal, and such alloys as have low melting points, flow out of the furnace, leaving materials which have higher melting points as a residue. This liquid product may be nearly pure or may contain several per cent of impurities such as lead, copper, bismuth, arsenic, and antimony. Tin may be refined by an electrolytic process in which large plates of the impure metal are the anodes and thin sheets of pure tin the cathodes. The electrolyte is an acidic solution of a stannous salt. Stannous ions are discharged at the cathode during electrolysis and are formed in equivalent concentration at the anode, while the other metals, less active than tin, remain undissolved.

Properties of Tin. The metal exists in three solid forms with definite transition temperatures. At ordinary temperatures, the stable form, β-tin, is a white crystalline metal which is very malle-

able and has little tensile strength. At 161°, there is a transition into another form, γ-tin. At temperatures below 18°, a gray modification, α-tin, is the stable form, but the rate of transition is slow and no considerable change occurs unless the metal is kept at a low temperature for a long time. Gray tin is very brittle and crumbles easily to a powder. The transition of the white into the gray tin is called "tin pest," because change spreads from a point of origin in a manner analogous to an infection in a plant or animal. White tin has a specific gravity of 7.28 and a melting point of 231.8°.

Reactions of Tin. Tin is not tarnished in air and it displaces hydrogen slowly from acids, such as hydrochloric acid, with the formation of stannous compounds.

$$Sn + 2\,H^+ \longrightarrow Sn^{++} + H_2$$
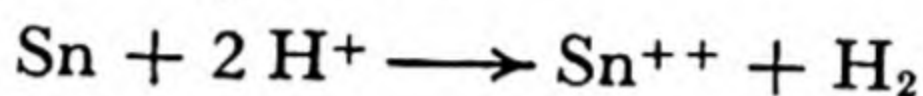
Tin reacts with solutions of sodium hydroxide to form the stannite ion and hydrogen.

$$Sn + 2\,H_2O + 2\,OH^- \longrightarrow Sn(OH)_4{}^{--} + H_2$$
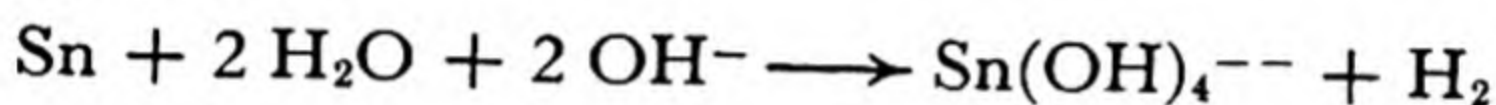
Reacting with concentrated nitric acid, tin yields the slightly soluble stannic acid, or hydrated stannic oxide, in which proportions of the oxide and water may vary. The stannate ion is most satisfactorily represented by the formula $Sn(OH)_6{}^{--}$ and the acid by the formula $H_2Sn(OH)_6$.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O] \times 4$$
$$\underline{[Sn + 6\,H_2O \longrightarrow H_2Sn(OH)_6 + 4\,H^+ + 4\,\epsilon] \times 3}$$
$$4\,H^+ + 4\,NO_3^- + 3\,Sn + 10\,H_2O \longrightarrow 4\,NO + 3\,H_2Sn(OH)_6$$
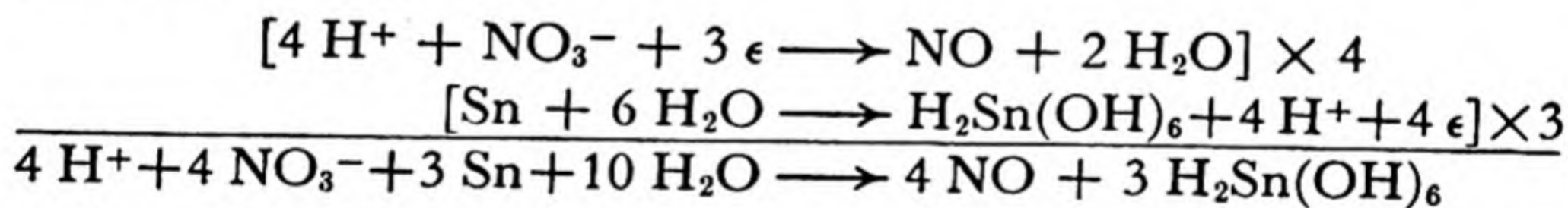
Uses of Tin. Large quantities of tin are used in the production of alloys. The approximate composition of some of these alloys is shown in Table 37.

TABLE 37. ALLOYS OF TIN

Name	Composition (Per Cent)
Britannia	Sn, 90–95; Sb, 5–10; Cu, 1–3
Babbitt	Sn, 70–90; Sb, 7–24; Cu, 2–22
Bell metal	Sn, 20–25; Cu, 75–80
Bronze	Sn, 15; Cu, 80; Zn, 5
Solder (medium)	Sn, 50; Pb, 50
Pewter (old)	Sn, 80; Pb, 20
Pewter (modern)	Sn, 85–90; Sb, 10–15
Aluminum solder	Sn, 86; Zn, 9; Al, 5
Type metal	Sn, 5–35; Sb, 8–20; Pb, 60–85
Wood's metal	Sn, 12.5; Pb, 25; Bi, 50; Cd, 12.5

The most extensive use of tin is normally in the production of tin-plate. Thin sheets of iron are cleaned by the action of dilute sulfuric acid to remove surface oxide. The cleaned metal is dipped into molten tin, and a thin coating of tin adheres to the iron. The most extensive use of tinplate is in the manufacture of tin cans for storing food and other materials. Iron is protected by the adhering layer of tin from the corrosive action of moisture and organic acids. Tin is used in manufacturing pipes and stills for distilled water. Tinfoil has many familiar uses, although, for many purposes, thin sheets of cellophane and other plastics are now used instead of tinfoil and other metal foils.

The Oxides and Hydroxides of Tin. *Stannous hydroxide,* $Sn(OH)_2$, is precipitated by the reaction of limited proportions of sodium hydroxide with a solution of stannous chloride. The precipitate may contain varying proportions of water, but is usually represented by the simple formula $Sn(OH)_2$.

$$Sn^{++} + 2\,OH^- \rightleftharpoons Sn(OH)_2 \downarrow$$
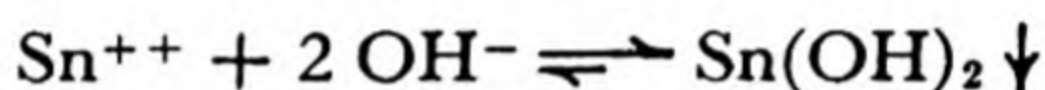
This hydroxide is amphoteric, reacting with an excess of hydroxide ions to form the stannite complex ion.

$$Sn(OH)_2 \downarrow + 2\,OH^- \rightleftharpoons Sn(OH)_4^{--}$$
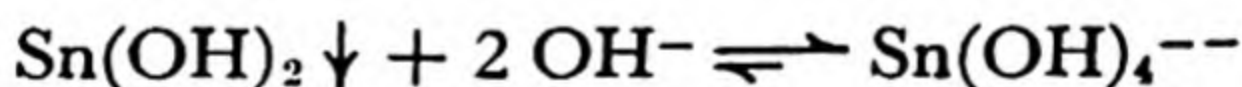
The stannite ion is an active reducing agent in basic solution.

Stannous oxide, SnO, may be formed by heating the hydroxide and by oxidizing the metal in a limited supply of air. This oxide burns in an excess of air to form the dioxide.

Tin dioxide, SnO_2, is formed by the combustion of the metal in an excess of air and by the dehydration of the hydrated oxide. Tin dioxide reacts with fused sodium hydroxide to form sodium stannate.

$$SnO_2 + 2\,NaOH \longrightarrow Na_2SnO_3 + H_2O$$
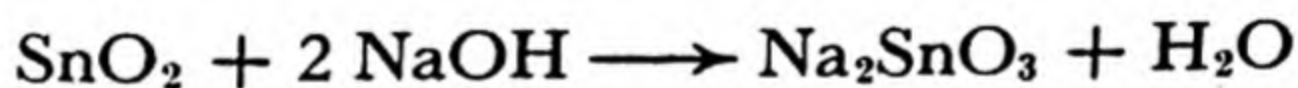
The salt is soluble in water and is decomposed by acids with the precipitation of α-stannic acid, an hydrous oxide represented by the specific formula $H_2Sn(OH)_6$.

$$SnO_3^{--} + 2\,H^+ + 3\,H_2O \longrightarrow H_2Sn(OH)_6 \downarrow$$
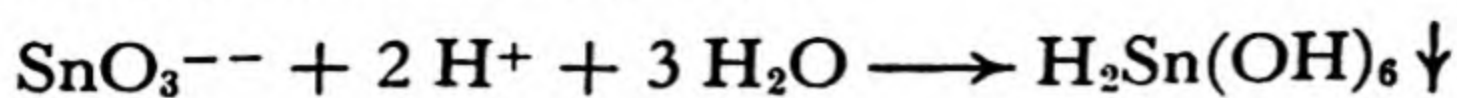
This hydrated oxide reacts with both acids and bases. Another form of the hydrous oxide, known as β-stannic acid, is formed by

the reaction of concentrated nitric acid with tin. This product dissolves in sodium hydroxide but does not dissolve in an excess of nitric acid. The differences in the behavior of the two forms are due to physical causes.

The Chlorides of Tin. *Stannous chloride*, **SnCl$_2$,** is formed by the reaction of tin with hydrochloric acid.

$$Sn + 2 H^+ \longrightarrow Sn^{++} + H_2$$
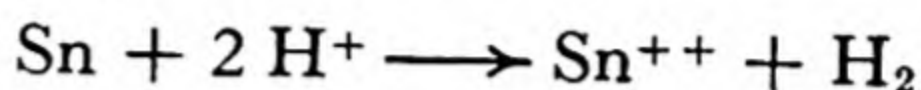
It is also formed by the reduction of the chlorostannate in acidic solution.

$$SnCl_6^{--} + Sn \longrightarrow 2 Sn^{++} + 6 Cl^-$$
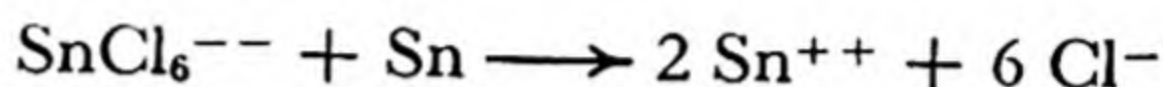
Stannous chloride hydrolyzes to form a precipitate of the hydroxy-chloride unless an excess of acid is present in the solution.

$$Sn^{++} + Cl^- + H_2O \rightleftharpoons SnOHCl \downarrow + H^+$$
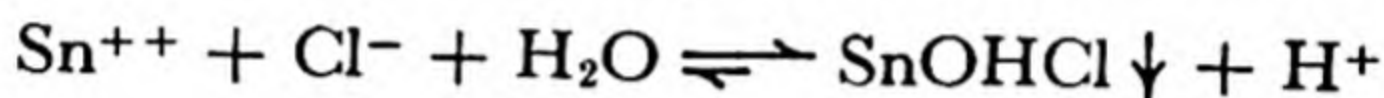
Stannous chloride becomes oxidized by oxygen absorbed from the air to form the stannic salt. Therefore, an excess of tin is kept in the bottles containing solutions of stannous chloride so that stannic compounds formed in this manner become reduced to stannous condition. Stannous chloride is used as a reducing agent. Ferric ions are reduced in acidic solution with the formation of ferrous ions.

$$2 Fe^{+++} + Sn^{++} + 6 Cl^- \longrightarrow 2 Fe^{++} + SnCl_6^{--}$$
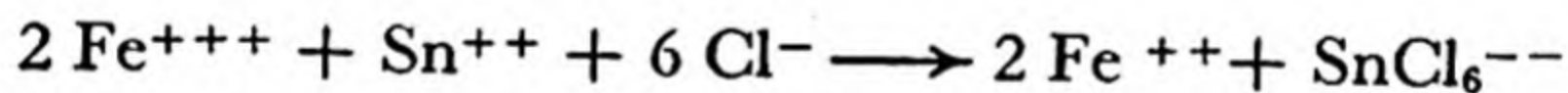
Stannic chloride, **SnCl$_4$,** is prepared commercially by heating tin with an excess of chlorine. Scrap tin may be detinned by reaction with chlorine at a pressure of about 4 atmospheres.

$$Sn + 2 Cl_2 \longrightarrow SnCl_4$$
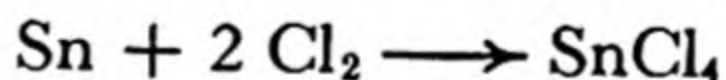
Stannic chloride is a colorless liquid that boils at 114°. It fumes in moist air, forming hydrogen chloride and hydrous stannic oxide.

$$SnCl_4 + 6 H_2O \longrightarrow 4 HCl + H_2Sn(OH)_6$$
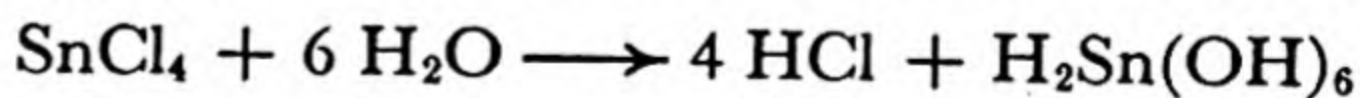
The complex chlorostannate ion is formed in solutions of stannic chloride that are acidic with hydrochloric acid, and the hydrated chloride, $SnCl_4(H_2O)_5$, may be crystallized from the acidic solution. Stannic chloride is used as a mordanting agent and as a fireproofing agent. Sodium stannate is formed by the reaction of this substance with sodium hydroxide. The fabric is soaked in a solution

of sodium stannate, dried, and then heated with a solution of ammonium sulfate. In this way stannic acid is formed in close contact with the fibers. Stannic acid adheres firmly to the fiber of the cloth and in turn adsorbs the dye.

Sulfides of Tin. Tin yields two sulfides, *viz.*, *brown stannous sulfide*, SnS, and *yellow stannic sulfide*, SnS_2. These sulfides may be formed by the direct union of the elements and also by the passage of hydrogen sulfide into solutions of stannous and stannic salts having the proper degree of acidity.

$$Sn^{++} + H_2S \rightleftharpoons SnS \downarrow + 2 H^+$$
$$SnCl_6^{--} + 2 H_2S \rightleftharpoons SnS_2 \downarrow + 4 H^+ + 6 Cl^-$$
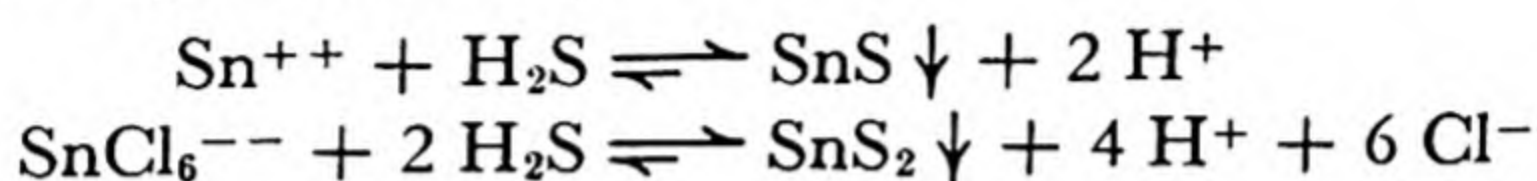
These sulfides are dissolved by concentrated hydrochloric acid. Stannic sulfide reacts with ammonium sulfide, and stannous sulfide with ammonium polysulfide, to form the complex thiostannate ion in solution.

$$SnS_2 + S^{--} \longrightarrow SnS_3^{--}$$
$$SnS + S_2^{--} \longrightarrow SnS_3^{--}$$
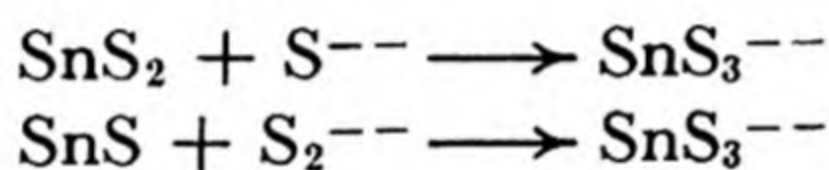
Stannic sulfide is used as a gilding pigment under the name *mosaic gold*. For this purpose, it is prepared by heating a mixture of tin and sulfur with ammonium chloride and mercury. The mercury and ammonium chloride are volatilized from this mixture, leaving stannic sulfide in a yellow crystalline form. The part that mercury and ammonium chloride play in this process is not definitely known.

LEAD

The most important ore of lead is *galena*, PbS. This ore occurs in large quantities in the United States, Mexico, Australia, and other countries. The ore second to galena in importance is *cerussite*, $PbCO_3$, which is a product of the natural oxidation of galena and is, therefore, known as an oxidized ore. Lead is produced from its ores in a number of states, Missouri, Idaho, and Utah being the leading producers.

The Production of Lead. Sulfide ores of lead often contain sulfides of other metals as well, *e.g.*, iron, copper, silver, bismuth, and arsenic. An outline of the essential steps in the production of lead from sulfide ores is shown in Fig. 123. If the ore contains

copper, additional steps involve the formation of a matte, composed primarily of copper and iron sulfides, which separates from
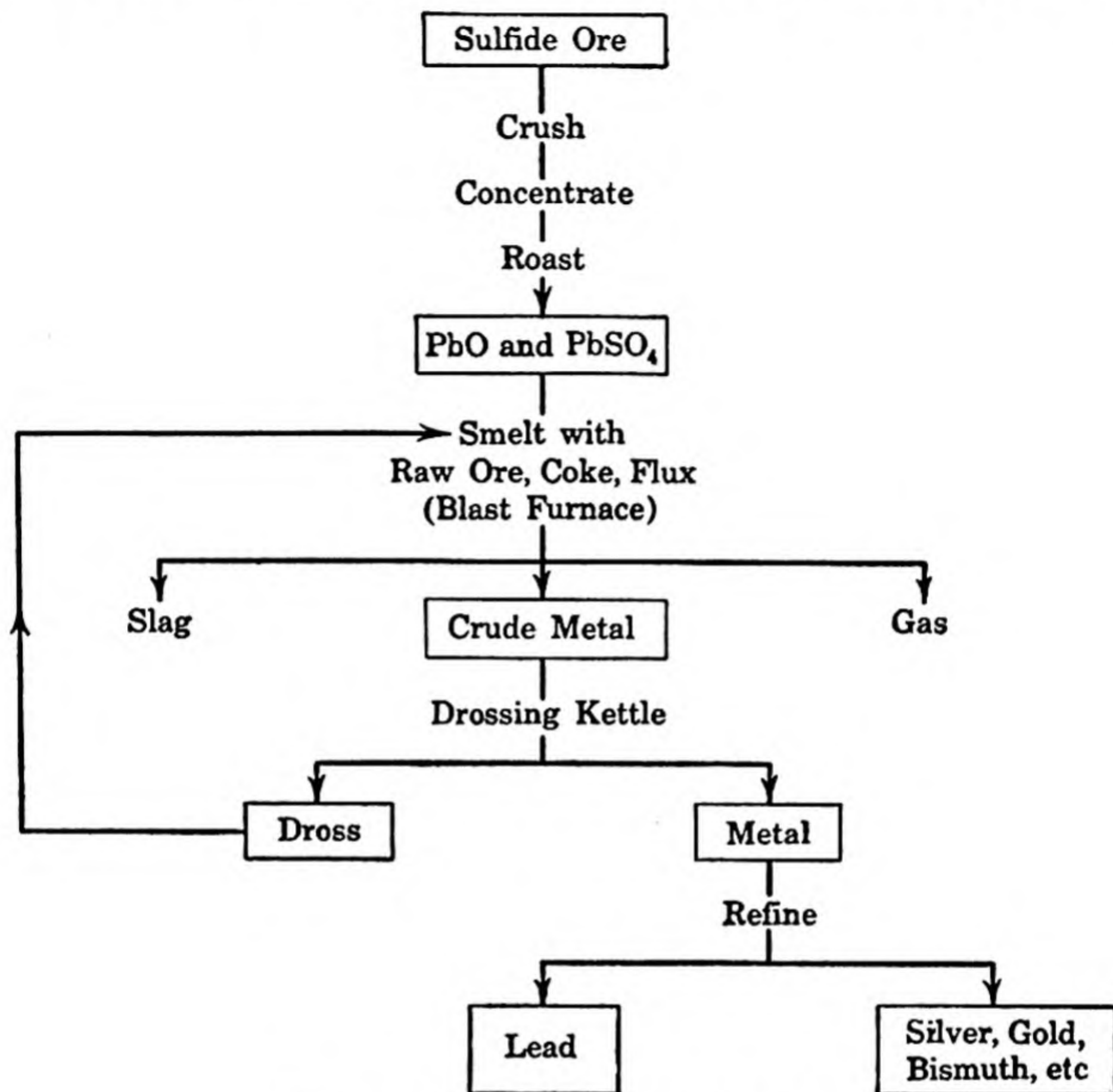
Fig. 123. Outline — Production of Lead

both metallic lead and slag. Lead sulfide is converted into the oxide and the sulfate during the roasting of the ore.

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$
$$PbS + 2\,O_2 \longrightarrow PbSO_4$$
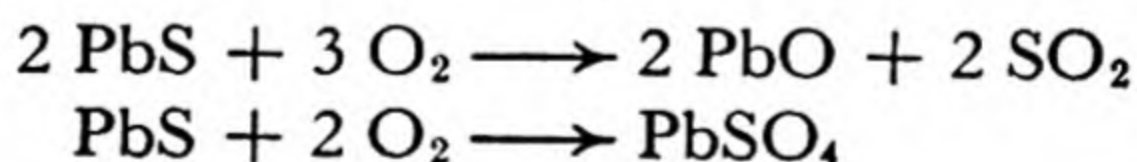
Pyrite is also oxidized to ferrous oxide and sulfur dioxide.

The blast furnace charge is a mixture containing the proper proportions of roasted ore, raw ore, coke, and flux, and sometimes scrap iron. The combustion of coke generates the heat for the process and also leads to the formation of carbon monoxide that serves as a reducing agent. There are a number of reactions in this process leading to the formation of lead, and those which follow are typical.

$$PbO + CO \longrightarrow Pb + CO_2$$
$$PbS + PbSO_4 \longrightarrow 2\,Pb + 2\,SO_2$$
$$PbS + Fe \longrightarrow Pb + FeS$$
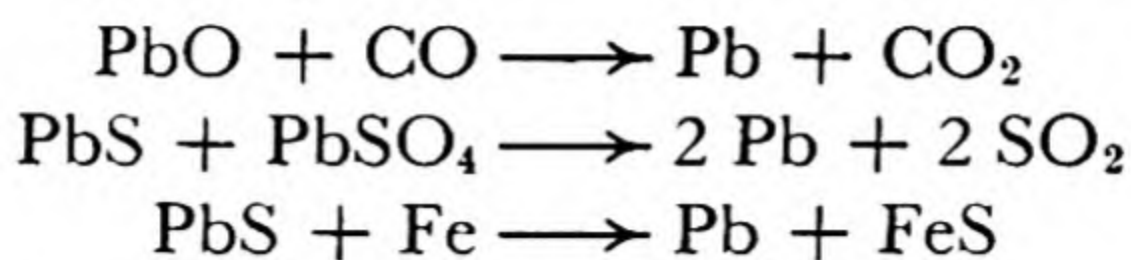
Slag formation results primarily from the reaction of silica and complex silicates with calcium oxide from the flux and with ferrous oxide from the roasted ore.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$FeO + SiO_2 \longrightarrow FeSiO_3$$
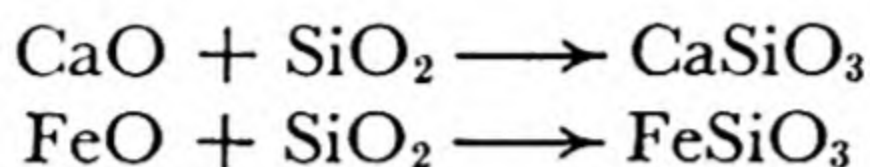
The slag and the metal are insoluble in each other and may be tapped separately from the furnace. Silver and gold, if present in the ore, are dissolved in the crude metal product.

The liquid metal is maintained at low temperature in the drossing kettle to allow impurities, dissolved in the metal at higher temperatures, to separate. Easily oxidizable substances are separated by stirring the molten lead in contact with air. The products formed in this manner rise to the surface and are skimmed off.

Silver and gold may be extracted from the molten lead by zinc in the *Parkes process*. Silver and gold are much more soluble in zinc than in lead, and zinc is only slightly soluble in lead. A small proportion of zinc is stirred into the melted lead and then allowed to rise to the surface and solidify. The zinc alloy is skimmed off, and zinc is distilled for repeated use. Silver and gold are extracted from the residue and refined. This process does not lead to the recovery of bismuth from the lead. Lead is usually refined by the *Betts electrolytic process* if the bismuth content is sufficient to justify the added cost. Plates of crude lead are the anodes, and sheets of pure lead the cathodes. The electrolyte is a solution of lead fluosilicate, $PbSiF_6$, containing free fluosilicic acid. Lead ions are discharged at the cathode during electrolysis and are formed by the oxidation of the anode. Metals, more active than lead, are also oxidized to form their ions at the anode but are not discharged at the cathode. Metals, less active than lead, fail to go into solution at the anode and form a sludge at the bottom of the tank. Silver, gold, and bismuth are recovered from the anode sludge.

Properties of Lead. Lead is a dense metal having a specific gravity of 11.34 at 20° and a melting point of 327.5°. It is malleable, but has little tensile strength. The metal is so soft that it can be

extruded through a die to form lead pipe. Lead may be hardened by alloying it with small proportions of antimony. The metal becomes superficially oxidized presenting a dull gray appearance, although a clean surface shows high luster.

Reactions of Lead. Lead reacts with oxygen to form the monoxide PbO at temperatures above 545°. It also reacts with the halogens and with sulfur.

$$Pb + Cl_2 \longrightarrow PbCl_2$$
$$Pb + S \longrightarrow PbS$$
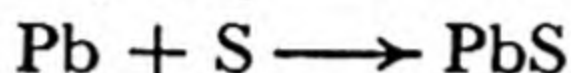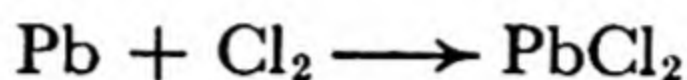
Although lead is above hydrogen in activity, it does not displace hydrogen readily from acidic solutions. It reacts with nitric acid and with acetic acid in the presence of oxygen of the air to form the soluble nitrate and acetate, respectively. Lead also reacts with sodium hydroxide solutions to form the plumbite complex ion and hydrogen.

$$Pb + 2\,H_2O + 2\,OH^- \longrightarrow Pb(OH)_4{}^{--} + H_2$$
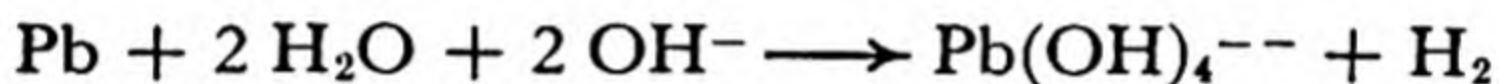
Pure water attacks lead, forming lead hydroxide which has low solubility and separates as a finely divided solid. If, however, carbonates, phosphates, or sulfates are present in the water, they react to form a protective coating. Soluble lead compounds are poisonous.

Uses of Lead. Lead is used widely in many industries. In addition to extensive production of lead from ores, a large quantity of lead is recovered from scrap and from discarded articles. The most extensive use of lead is in the manufacture of storage battery plates. An alloy containing 5–12 per cent of antimony is used for this purpose because of its greater strength and hardness. Large quantities of lead are used in the production of lead hydroxycarbonate, called *basic carbonate of lead*, a pigment in white paint. The metal with about 1 per cent of antimony is extensively used in cable coverings for telephone wires. Lead is also used in shot, pipes, foil, and in lining chambers for the production of sulfuric acid. There are a number of important alloys of lead, *e.g.*, solder, type metal, pewter, and Wood's metal, an alloy of low melting point. The composition of these alloys is shown in Table 37, page 471.

The Oxides and Hydroxides of Lead. *Lead monoxide, litharge,* **PbO,** is prepared by heating lead in a current of air at a

temperature above 545°. It is also produced by heating lead with sodium nitrate.

$$Pb + NaNO_3 \longrightarrow PbO + NaNO_2$$
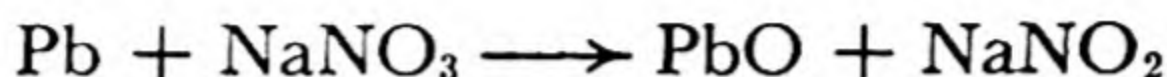
This oxide reacts with acids to form electrovalent lead ions and with solutions of basic hydroxides to form plumbite ions.

$$PbO + 2\,H^+ \longrightarrow Pb^{++} + H_2O$$
$$PbO + H_2O + 2\,OH^- \longrightarrow Pb(OH)_4{}^{--}$$
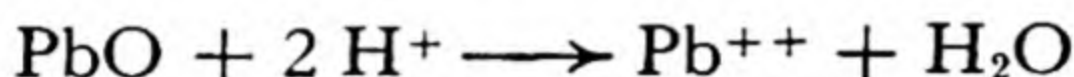
Soluble lead salts react with limited proportions of sodium hydroxide to form a gelatinous precipitate of the hydrous oxide, commonly represented by the simple formula $Pb(OH)_2$.

$$Pb(H_2O)_4{}^{++} + 2\,OH^- \rightleftharpoons Pb(H_2O)_2(OH)_2 \downarrow + 2\,H_2O$$
or $$Pb^{++} + 2\,OH^- \rightleftharpoons Pb(OH)_2 \downarrow$$
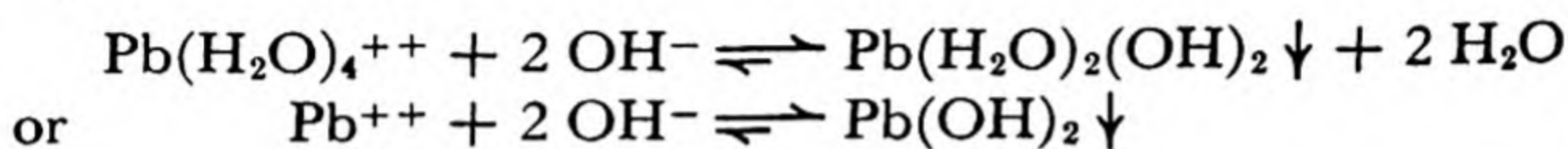
This hydroxide reacts with an excess of sodium hydroxide to form the plumbite. Litharge is used in glazing pottery, in the rubber industry, and in the manufacture of glass and enamels. A mixture of litharge and glycerol forms a good cement for glass and stoneware.

Lead dioxide, PbO₂, may be prepared by the oxidation of a plumbite by sodium hypochlorite in basic solution.

$$ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-$$
$$\underline{Pb(OH)_4{}^{--} \longrightarrow PbO_2 + 2\,H_2O + 2\,\epsilon}$$
$$ClO^- + Pb(OH)_4{}^{--} \longrightarrow Cl^- + PbO_2 + 2\,OH^- + H_2O$$
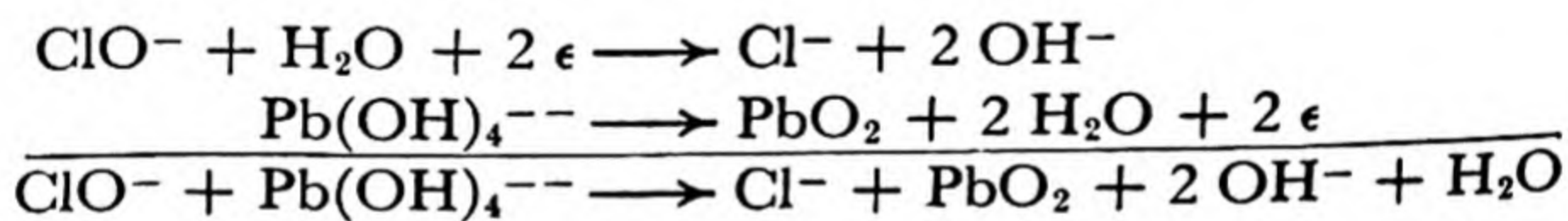
It is an acidic oxide that reacts with concentrated solutions of strong bases to form plumbates but does not react with water. Lead dioxide is a strong oxidizing agent in acidic solutions. The role of this oxide in storage batteries is discussed in Chapter 15, page 243.

Red lead, minium, Pb₃O₄, is prepared by heating lead monoxide in air at temperatures below 500°. The composition of the product varies at different temperatures. The product at 430° has the composition represented by the formula Pb_3O_4. This compound reacts with nitric acid, with the formation of lead nitrate and the precipitation of lead dioxide.

$$4\,H^+ + Pb_3O_4 \longrightarrow 2\,Pb^{++} + PbO_2 + 2\,H_2O$$
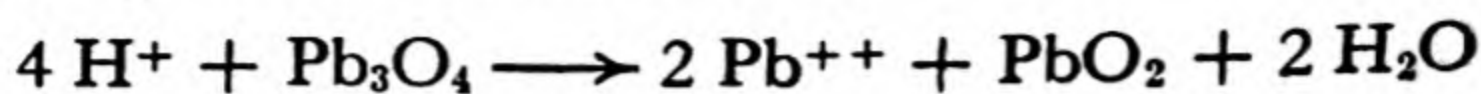
This reaction indicates that two thirds of the lead in red lead is divalent and basic in nature, while the remainder is tetravalent and acidic. Consequently, the compound is considered to be a slightly soluble salt represented by the formula Pb_2PbO_4. This oxide is used in making flint glass and as a pigment in red paint, such as that used for the first coat on structural iron and steel.

Soluble Lead Salts. The common soluble lead salts are the nitrate and the acetate. *Lead nitrate*, $Pb(NO_3)_2$, is prepared by the reaction of nitric acid with lead or lead oxide.

$$[4 H^+ + NO_3^- + 3 \epsilon \longrightarrow NO + 2 H_2O] \times 2$$
$$\underline{[Pb \longrightarrow Pb^{++} + 2 \epsilon] \times 3}$$
$$8 H^+ + 2 NO_3^- + 3 Pb \longrightarrow 2 NO + 3 Pb^{++} + 4 H_2O$$
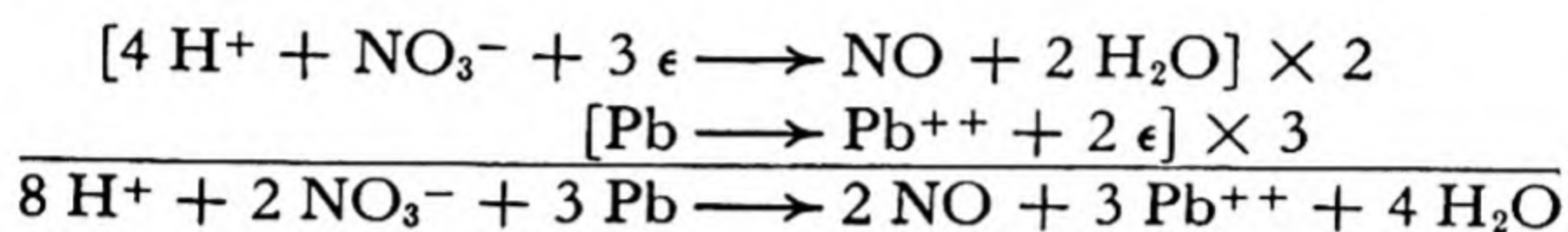
Lead acetate, $Pb(C_2H_3O_2)_2$, is prepared by the reaction of lead with acetic acid in the presence of oxygen.

$$2 Pb + 4 HC_2H_3O_2 + O_2 \longrightarrow 2 Pb(C_2H_3O_2)_2 + 2 H_2O$$

Lead acetate is soluble in water but yields only low concentrations of lead ions, due in part at least to the formation of complex ions with an excess of acetate ions.

$$Pb^{++} + 4 C_2H_3O_2^- \rightleftharpoons Pb(C_2H_3O_2)_4^{--}$$
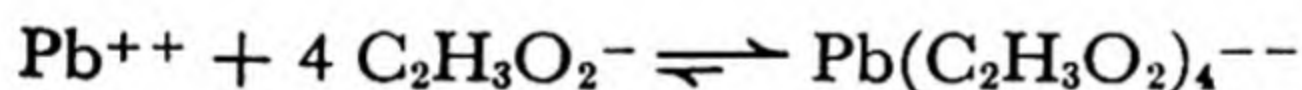
Lead ions hydrolyze with the formation of lead hydroxy complex ions, unless an excess of acid is maintained in the solution.

$$Pb(H_2O)_4^{++} + H_2O \rightleftharpoons Pb(H_2O)_3OH^+ + H_3O^+$$
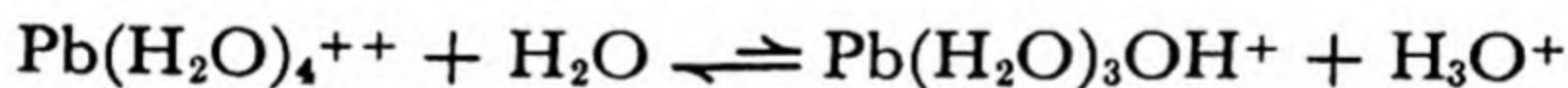
Slightly Soluble Lead Salts. Lead yields salts with a number of the common anions. Most of these salts have low solubility, with the exception of the nitrate, acetate, and fluosilicate. The common slightly soluble lead salts are the chloride, sulfide, sulfate, carbonate, and chromate. Usually, these salts are prepared by precipitation. The solubility of *lead chloride*, $PbCl_2$, is sufficiently great to prevent its precipitation with low concentrations of its ions. The solubility of this salt increases greatly with rise in temperature. It reacts with a high concentration of chloride ions, with the formation of the chloroplumbate complex ion.

$$PbCl_2 + 2 Cl^- \rightleftharpoons PbCl_4^{--}$$
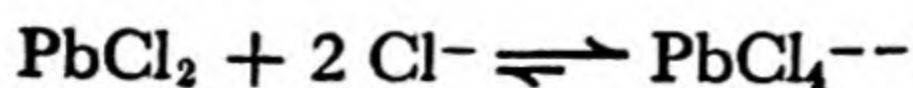
Lead chromate, **PbCrO₄,** is a yellow salt, important as the paint pigment, *chrome yellow.* The salt may be precipitated from weakly acidic solutions.

$$Pb^{++} + CrO_4^{--} \rightleftharpoons PbCrO_4 \downarrow$$
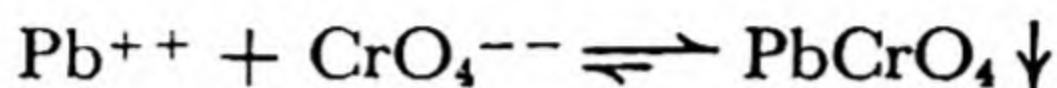
It dissolves in strongly acidic solutions, because of the conversion of chromate into dichromate ions.

$$2\,CrO_4^{--} + 2\,H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$

The concentration of chromate ions represented in this equilibrium is so low that

$$[Pb^{++}] \times [CrO]_4^{--} < S_{PbCrO_4}$$
$$PbCrO_4 \downarrow + 2\,H^+ \longrightarrow Pb^{++} + Cr_2O_7^{--} + H_2O$$
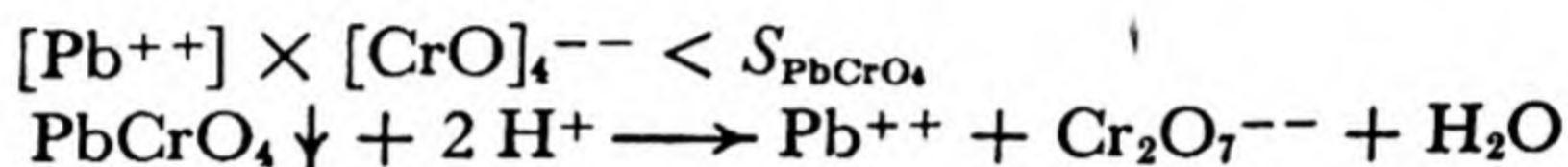
Lead sulfate, **PbSO₄,** resembles the sulfates of barium and strontium in solubility.

$$Pb^{++} + SO_4^{--} \rightleftharpoons PbSO_4 \downarrow$$
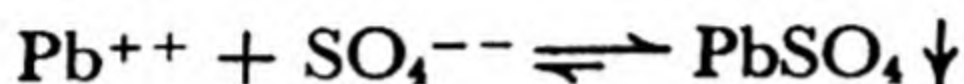
This substance is dissolved by a solution containing a high concentration of acetate ions, forming the weakly dissociated complex acetate ion. The concentration of simple lead ions is reduced so greatly by the formation of this complex ion that the product of the molar concentrations of the ions is made less than the solubility product.

$$PbSO_4 \downarrow + 4\,C_2H_3O_2^- \rightleftharpoons Pb(C_2H_3O_2)_4^{--} + SO_4^{--}$$
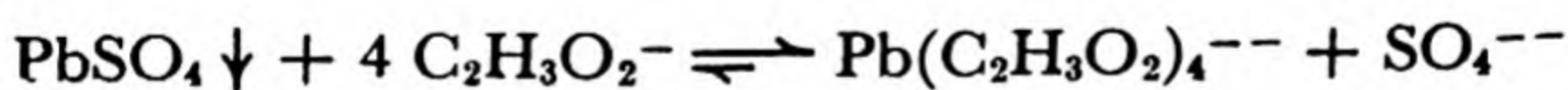
An oxysulfate of lead, Pb₂OSO₄, basic lead sulfate, may be produced by roasting lead sulfide at a high temperature in a current of air admitted at a controlled rate. The oxysulfate sublimes from the mixture and condenses to form a white powder, which is used in paint. This pigment is not poisonous.

Lead hydroxycarbonate, basic lead carbonate, **(PbCO₃)₂Pb(OH)₂,** is precipitated by the reaction of sodium carbonate with lead nitrate in solution. In the "old Dutch process" for the manufacture of white lead, perforated disks of lead are placed over small amounts of acetic acid in earthenware pots. These pots are placed on layers of moist tanbark. A board floor is supported a few inches above the layer of pots and successive layers are similarly arranged until the room is full. The fermentation of the tanbark produces

carbon dioxide, and heat is generated. Vapors from acetic acid slowly react with the lead to form basic lead acetate, which reacts with carbon dioxide to form the basic lead carbonate. At the conclusion of the process, the basic lead carbonate is separated from any fragments of unchanged lead and ground with linseed oil.

In addition, basic lead carbonate is made by an electrolytic process. In this process the anodes are lead and the cathodes iron. A diaphragm about the cathode divides the cell so that the electrolytes around the two electrodes are separated, except for ionic migration through the diaphragm. Both solutions contain sodium acetate, and the anode liquid contains a few tenths of 1 per cent of sodium carbonate, while the cathode liquid contains as much as 5 per cent. During electrolysis, lead dissolves at the anode to form lead acetate, which diffuses away from the anode and comes in contact with carbonate ions electrolytically attracted toward the anode. The reaction of these two materials causes the precipitation of basic lead carbonate.

Paint consists of a quick-drying oil, a material to give good covering power, an inert filler, and a color pigment if a colored paint is desired. The most extensively used drying oil, *the vehicle*, is linseed oil. It "dries" due to oxidation, forming a tough film which adheres to the wood and protects it. *Driers*, such as oxides of manganese, nickel, and cobalt, are sometimes added to catalyze the oxidation reaction and hasten the drying. Such substances are used particularly in paint for inside work, shielded from the action of sunlight. Covering power is secured by the use of a substance, *the body*, which readily reflects light. This makes the paint opaque. Basic lead carbonate is used extensively, because it gives the paint good covering power. Basic lead sulfate, lithopone, titanium dioxide, and zinc white are also used as the body in paints. Zinc white is used extensively in interior work and in other places where the paint is likely to be exposed to air containing hydrogen sulfide. Hydrogen sulfide reacts slowly with the basic ingredients of paint and causes lead white to darken, due to the formation of lead sulfide which is black. Zinc sulfide is white, and the reaction of hydrogen sulfide with zinc white does not cause darkening. The *filler* is added to the paint to prevent too thin a coating. Various oxides and other colored substances are used as pigments.

EXERCISES

1. Discuss structural similarities and differences among the elements of Group IV.
2. Describe the production of tin from its oxide ore.
3. Represent by equations reactions of tin with (a) chlorine, (b) oxygen, (c) hydrochloric acid, (d) sodium hydroxide, and (e) nitric acid.
4. List uses of tin which indicate its industrial importance.
5. Represent by equations reactions of stannous compounds, as reducing agents in both basic and acidic solution.
6. List important ores of lead, and describe methods for the production of the metal from sulfide ores.
7. Describe the Parkes process for the extraction of gold and silver from lead.
8. Describe the electrolytic process for the refining of lead, and explain how it effects the separation of different types of impurities.
9. Indicate by equations the important reactions of lead.
10. What are the ingredients of a good white paint for the outside walls of a house? What is the function of each of these? What changes in composition are made in preparing a paint for inside use? Explain.
11. Indicate by equations the reactions that may be employed for the production of (a) lead monoxide, (b) red lead, (c) lead nitrate, (d) stannic chloride, (e) chlorostannic acid.
12. Discuss and illustrate by equations the hydrolysis of (a) stannous chloride, (b) stannic chloride, (c) sodium stannite.

SUPPLEMENTARY READINGS

Hayward, C. R., *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1929, chaps. II, VI.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chap. 31.

Furnas, C. C., *Rogers Manual of Industrial Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, chap. 26.

"White Lead Process," Pictured Flow Sheet, *Chem. Met. Eng.* 50, 3, 130 (1943).

Chapter 30

COPPER. SILVER. GOLD

These elements are the transition elements of Group I–B. Their atoms contain one valence electron, but the atomic kernels differ from the inert gas structure, since the outermost shell contains eighteen electrons instead of eight. Therefore, in each transition series with increase in the atomic number, the outer shell of the atomic kernel is completed in the element in this group. The metals of Group I–B yield ions having an electrovalence of 1 +, but the atoms may also lose additional electrons from the next lower shell to form ions with higher electric charges. The metals have low activity, and gold, the element with the highest atomic number in the group, is the least active. The hydroxides are only weakly basic, and the ions of these metals form complex ions readily. The metals have relatively high melting points and high density. Some of the properties of these elements are listed in Table 39.

TABLE 39. PROPERTIES OF COPPER, SILVER, AND GOLD

Property	Copper	Silver	Gold
Atomic weight	63.57	107.88	197.20
Atomic number	29	47	79
Isotopes	63, 65	107, 109	197
Electron structure	2, 8, 18, 1	2, 8, 18, 18, 1	2, 8, 18, 32, 18, 1
Oxidation numbers	1 +, 2 +	1 +, 2 +	1 +, 2 +, 3 +
Melting point (° C.)	1083.0	960.5	1063.0
Density at 20°, g. per ml.	8.92	10.50	19.30

COPPER

Copper was one of the first metals used by primitive man. Implements of uncertain date, made of this metal, have been discovered. The Egyptians, Babylonians, and Assyrians made extensive use of copper and had developed a high degree of skill in working and shaping it.

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Ores of Copper. The most important ores of copper are the sulfide ores, *e.g.*, *chalcopyrite*, $CuFeS_2$, *chalcocite*, Cu_2S, and *covellite*, CuS. In the United States, the largest deposits of these ores are

```
                    ┌─────────────┐
                    │ Sulfide Ore │
                    └─────────────┘
                          │
                        Crush
                          │
                     Concentrate
                     (Flotation)
                          ↓
                  ┌──────────────────┐
                  │ Concentrated Ore │
                  │  ( 20 - 30% Cu)  │
                  └──────────────────┘
                          │
                    Roast, Partial
                          │
             (Reverberatory Furnace)
                  Limestone Flux
```
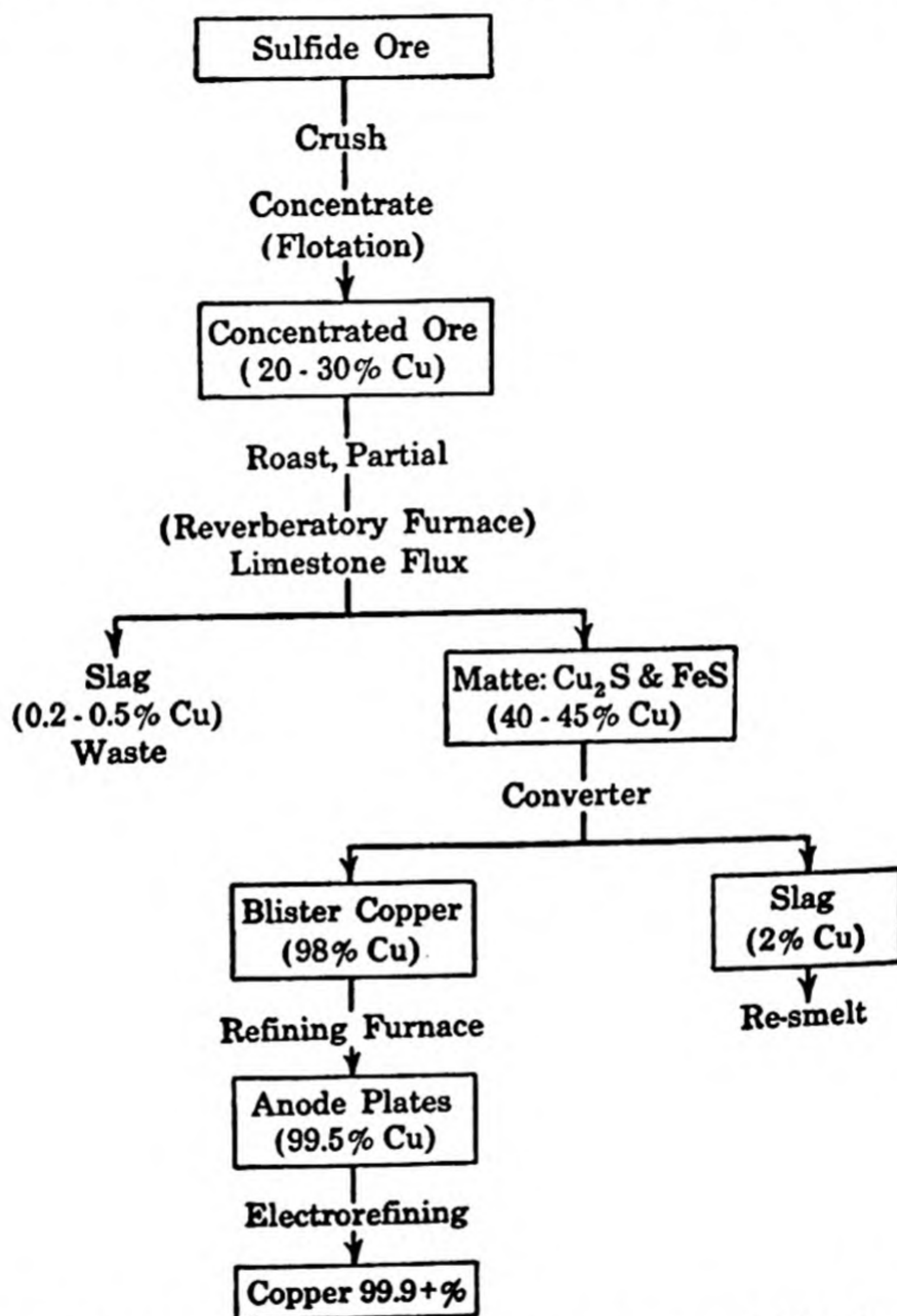

Fig. 124. Outline — Production of Copper from Sulfide Ores

in Montana, Utah, Nevada, Arizona, and New Mexico. The important oxidized ores are *malachite*, $CuCO_3Cu(OH)_2$, and *azurite*, $(CuCO_3)_2Cu(OH)_2$, found in Arizona and New Mexico. *Native copper* occurs as an important ore in the upper peninsula of Michigan.

Production of Copper from Sulfide Ores. Approximately 70 per cent of the copper produced in the United States comes from

sulfide ores. The procedure for the extraction of the metal is complicated by the fact that the ores always contain iron and several other metals. The per cent of copper in many of the ores is only 1–3. An outline of the general steps involved in the production of the metal from the sulfide ores is shown in Fig. 124.

The concentrated ore is roasted to burn out a large proportion of the sulfur, leaving enough to hold all the copper and a portion of the iron in combination when the materials are fused in the next step of the procedure. The roasted ore contains sulfides, oxides, and sulfates of copper and iron together with silica and complex silicates. It is smelted in a reverberatory furnace with limestone as a flux. The stability of cuprous sulfide is so great that the other compounds of copper are changed into the sulfide. Cuprous oxide, for example, reacts with some of the unchanged ferrous sulfide, with the formation of cuprous sulfide.

$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$
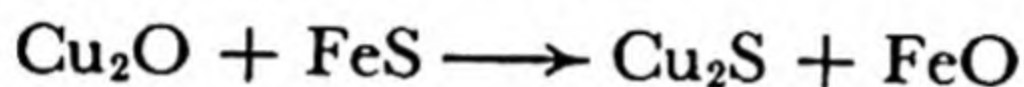
The excess of sulfur, over that required by the copper, holds some of the iron in combination as ferrous sulfide. Silica and complex silicates react with ferrous oxide and with the flux to form a silicate slag.

$$FeO + SiO_2 \longrightarrow FeSiO_3$$
$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$
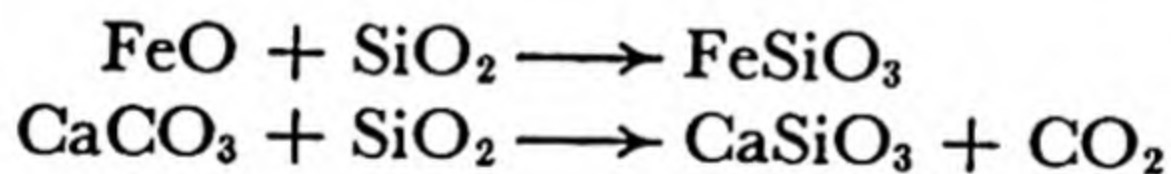
Cuprous sulfide and ferrous sulfide melt to form *matte*, a solution of these sulfides in each other. Since the molten matte and slag do not dissolve in each other, they are easily separated. Matte contains gold, silver, bismuth, arsenic, lead, and zinc, either as uncombined metals or as sulfides, if these metals are present in the ore.

The formation of *blister copper* from matte is accomplished by burning out the sulfur in large converters, made of steel plate and lined with heat resistant magnesia brick. The converter is mounted on trunnions so that it may be tilted to different positions for the introduction of the charge, for the air blast, and for the pouring of the products. A number of steel pipes, approximately 1.5 in. in diameter, known as tuyères, lead in, at the base of the converter wall, to admit the air blast. In the process, known as *bessemerizing*, ferrous sulfide is burned to oxide and sulfur dioxide before cuprous

sulfide burns. The correct quantity of silica is added to react with ferrous oxide and form a slag.

$$2\,FeS + 3\,O_2 \longrightarrow 2\,FeO + 2\,SO_2$$
$$FeO + SiO_2 \longrightarrow FeSiO_3$$
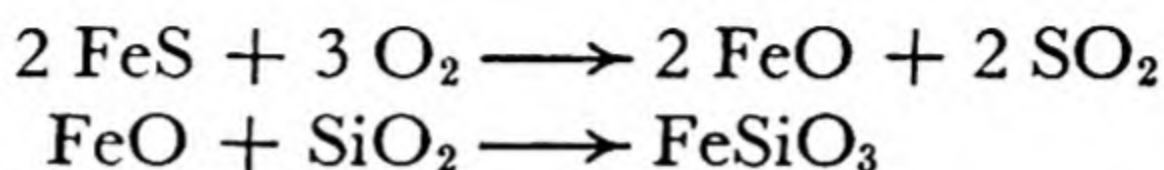
When all the ferrous sulfide has been oxidized, the air blast is discontinued, and the converter is tilted to pour out the slag. It is then turned back to the blowing position, and the air blast is renewed. Cuprous sulfide now burns to form copper and sulfur dioxide.

$$Cu_2S + O_2 \longrightarrow 2\,Cu + SO_2$$
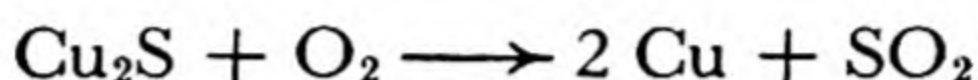
Some of the sulfide may be oxidized to cuprous oxide, but except toward the end of the operation, most of the oxide formed in this manner is reduced by some of the unchanged sulfide.

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2$$
$$2\,Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2$$
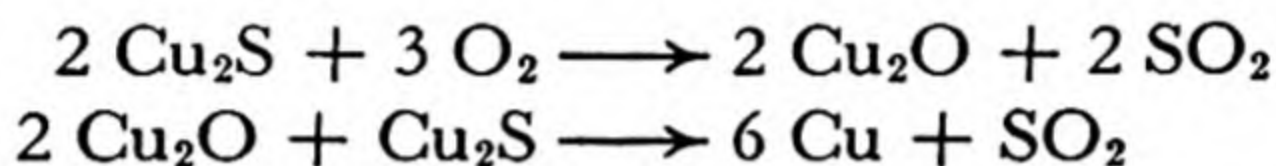
The converter handles a charge of approximately 65 tons and the "blow" requires approximately five hours. The escape of sulfur dioxide from the metal causes it to have a blistered appearance. This product may contain 1–3 per cent of impurities, such as silver, gold, bismuth, and some sulfur and iron. The product is porous and brittle so that it requires further treatment.

Blister copper may be further refined in a reverberatory furnace by first oxidizing the remaining sulfur and iron, and then reducing the cuprous oxide dissolved in copper. This metal is pure enough for many uses. Further refining is done by an electrolytic process if the crude metal contains silver and gold and if a product of high purity is required. Electrorefining eliminates arsenic which greatly decreases the electrical conductivity of copper.

Production of Copper from Oxidized Ores. Copper may be produced by reducing the oxidized ores by coke or coal in a reverberatory furnace or in a blast furnace. This process is wasteful, for the loss of copper in the slag is high. The better practice is to mix the oxidized ore with sulfide ore and to smelt in a reverberatory furnace to form a matte.

Production of Copper from Native Ores. The ores are crushed in stamp mills, and a large proportion of the finely divided silica

is washed away by water. The concentrates are smelted with a flux in a reverberatory furnace, as described in Chapter 26, page 431. The crude metal is refined, as described for blister copper.

The Leaching of Low Grade Ores. The extraction of copper from low grade ores is brought about by leaching out the copper and copper compounds. Different substances are used as leaching solutions, depending on the type of ore being treated. Native copper may be leached from the finely ground ore, and from the discarded sands from the concentration process, by an ammoniacal solution of cupric ammonia carbonate, forming a solution of cuprous ammonia carbonate.

$$Cu + Cu(NH_3)_4{}^{++} \longrightarrow 2\,Cu(NH_3)_2{}^+$$
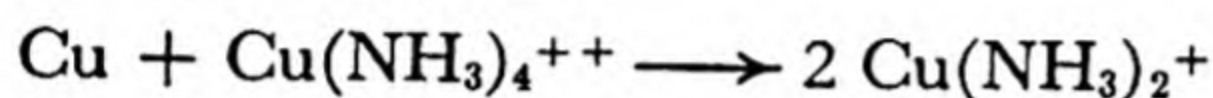
A precipitate of copper hydroxycarbonate and copper oxide is obtained when ammonia is boiled out of this solution. This residue may be smelted by reduction with carbon to form the metal. Copper may be extracted from oxidized ores by reaction with dilute sulfuric acid.

$$CuCO_3 + 2\,H^+ \longrightarrow Cu^{++} + CO_2 + H_2O$$
$$Cu(OH)_2 + 2\,H^+ \longrightarrow Cu^{++} + 2\,H_2O$$
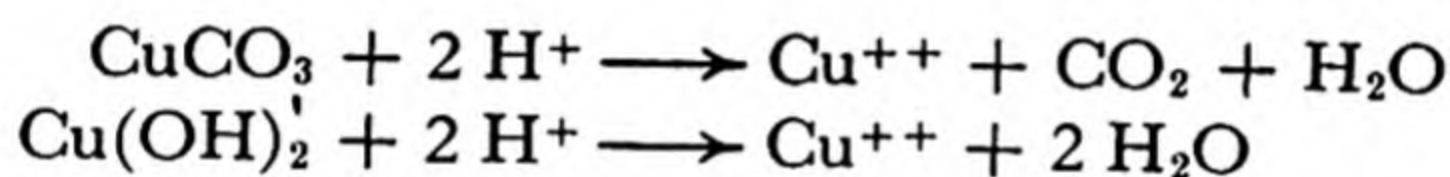
Copper sulfide ores may be leached with a solution of sulfuric acid containing ferric sulfate as an oxidizing agent, producing a solution of cupric and ferrous sulfates.

$$CuS + 2\,Fe^{+++} \longrightarrow Cu^{++} + 2\,Fe^{++} + S$$
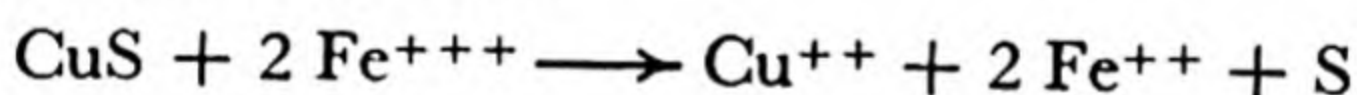
Copper may be recovered from this solution of cupric sulfate by displacing the metal with scrap iron and by electrolysis
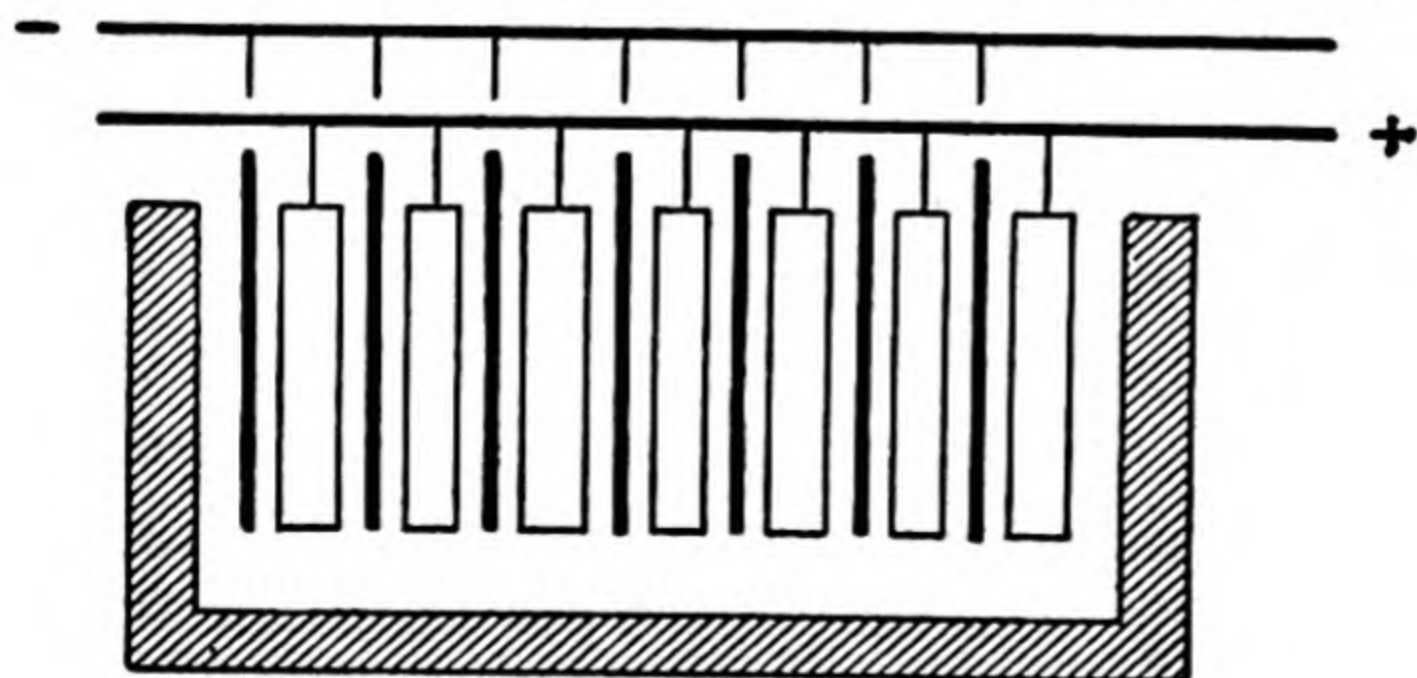
Fig. 125. Diagram. Refining of Copper

Electrorefining of Copper. The copper to be refined is cast into large plates, approximately 3 ft. square and 2 in. thick. These plates

are the anodes, and the electrolyte is a solution of cupric sulfate which is acidic with sulfuric acid. Thin sheets of pure copper are placed alternately with the anode plates to serve as cathodes. (Fig. 125.)

During the passage of the current, cupric ions from the electrolyte are reduced by the gain of electrons at the cathode and are deposited as metallic copper, so that the cathodes gradually build up.

$$Cu^{++} + 2\,\epsilon \longrightarrow Cu$$
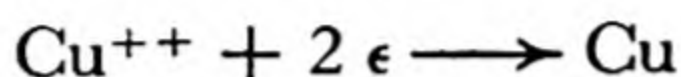
An equivalent number of positive ions, chiefly cupric, are formed at the anode, so that the concentration of the solution is not greatly changed.

$$Cu \longrightarrow Cu^{++} + 2\,\epsilon$$

Metals more active than copper, such as iron and nickel, also dissolve at the anode, but they are not deposited at the cathode.

$$Fe \longrightarrow Fe^{++} + 2\,\epsilon$$

Lead also dissolves and is removed from the solution by the precipitation of lead sulfate.

$$Pb + SO_4^{--} \longrightarrow PbSO_4 \downarrow + 2\,\epsilon$$
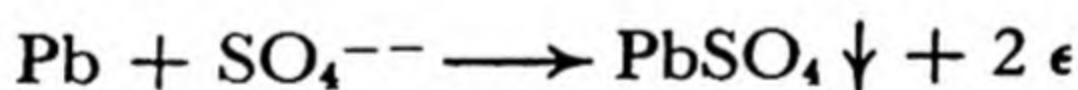
The oxidation of arsenic at the anode yields arsenious acid, which partly precipitates in the form of arsenites in the anode mud and partly remains in the solution. Gold and silver, being less active than the copper, do not dissolve at the anode but settle to the bottom as they are dislodged by the wearing away of the anode, and they are present in the anode mud. The purity of the electrolytically refined copper is 99.94–99.98 per cent. Gold, silver, and other substances of value, such as arsenic, selenium, and tellurium, are obtained from the anode mud.

In the electrolytic refining of copper, only a low potential difference is required. The composition of the vat liquid is not materially changed during the process, and the composition of the crude anode differs so little from that of the pure cathode that there is but little reverse potential to be overcome.

Properties and Reactions of Copper. Copper is a reddish brown metal with a moderately high melting point, 1083°. It is very malleable and ductile and is the best conductor of heat and elec-

tricity among the cheap metals. Copper does not combine actively with oxygen at low temperatures but reacts to form cupric oxide when heated with an excess of air.

$$2\,Cu + O_2 \longrightarrow 2\,CuO$$
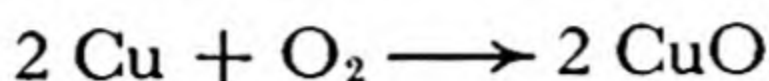
Cuprous sulfide is produced by the reaction of copper with sulfur, even though an excess of sulfur may be used.

$$2\,Cu + S \longrightarrow Cu_2S$$
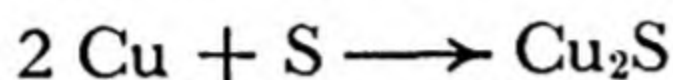
Copper slowly becomes coated with a film of the hydroxycarbonate when exposed to moist air containing carbon dioxide, thus causing the green color observed on many copper roofs. The hydroxysulfate of copper is formed in moist air containing sulfur dioxide. This product dissolves in dilute solutions of sulfuric acid. Copper gutters and leaders may corrode quickly because of the sulfur dioxide introduced into the air by the combustion of fuels that contain sulfur. Copper does not displace hydrogen from acids but does react with acidic oxidizing agents, such as nitric acid and hot concentrated sulfuric acid and with dilute sulfuric acid in contact with the oxygen of the air.

Uses of Copper. The most important uses of copper, based on its high conductivity of electricity, are in electrical machinery, light and power lines, and in telephone and telegraph wires and cables. Large quantities of the metal are used in the production of important alloys such as those listed in Table 40.

TABLE 40. ALLOYS OF COPPER

Name	*Composition (Per Cent)*
Aluminum brass	Cu, 68–70; Zn, 27–31; Al, 1–3
Aluminum bronze	Cu, 90; Al, 10
Babbitt metal	Cu, 2–22; Sn, 70–90; Sb, 7–24
Bell metal	Cu, 75–80; Sn, 20–25
Brass	Cu, 60–90; Zn, 10–40
Britannia metal	Cu, 1–3; Sn, 90–95; Sb, 5–10
Bronze	Cu, 80; Sn, 15; Zn, 5
Constantan	Cu, 60; Ni, 40
Gold coin	Cu, 10; Au, 90
Gun metal	Cu, 90; Sn, 10
Manganese bronze	Cu, 70–95; Mn, 5–30
Manganin	Cu, 82; Mn, 15; Ni, 3
Monel metal	Cu, 36; Ni, 60; Fe, 3.5; Al, 0.5
Nickel silver	Cu, 55; Ni, 20; Zn, 25
Silver coin	Cu, 10; Ag, 90
Silver (sterling)	Cu, 7.5; Ag, 92.5

Since copper is a good conductor of heat and is not readily corroded by air, it is used in boilers, water heaters, and cooking utensils. The metal is a so employed in the manufacture of roofing shingles and gutters, the sheathing of boats, and for a variety of familiar purposes. Metals which corrode easily may be protected with a film of copper, deposited in an electrolytic process similar to the refining of copper. Electrotypes are made in a similar manner by making a cast of the object, coating it with graphite to give electrical conductivity, and using the prepared cast as the cathode in an electroplating cell.

Compounds of Copper. Copper forms ions in two states of oxidation. *Cupric ions*, Cu^{++}, are formed by the vigorous oxidation of copper with strong oxidizing agents such as the halogens and nitric acid. *Cuprous ions*, Cu^+, result from the mild reduction of cupric ions. Both cuprous and cupric ions yield a number of complex ions, *e.g.*, cuprous ammonia, $Cu(NH_3)_2^+$, cuprocyanide, $Cu(CN)_2^-$, cuprochloride, $CuCl_2^-$, cupric ammonia, $Cu(NH_3)_4^{++}$, cupric hydrate, $Cu(H_2O)_4^{++}$, chlorocuprate, $CuCl_4^{--}$, and the tartrate, $Cu(C_4H_4O_6)_2^{--}$. The common soluble cupric salts are the chloride, the sulfate, and the nitrate. Solutions of these salts are acidic, because they contain the cation acid, $Cu(H_2O)_4^{++}$.

$$Cu(H_2O)_4^{++} + H_2O \rightleftharpoons Cu(H_2O)_3OH^+ + H_3O^+$$
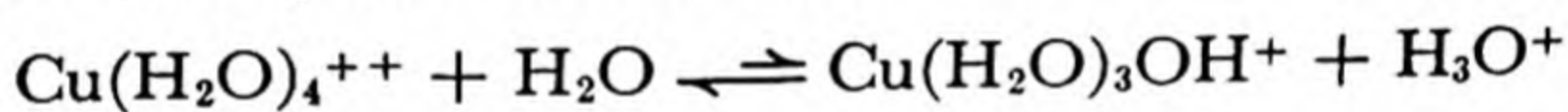
Oxides and Hydroxides of Copper. *Cupric hydroxide*, $Cu(OH)_2$, is formed as a blue gelatinous precipitate by the reaction of a sodium hydroxide solution with a soluble cupric salt.

$$Cu(H_2O)_4^{++} + 2\,OH^- \rightleftharpoons Cu(H_2O)_2(OH)_2 \downarrow + 2\,H_2O$$
or $$Cu^{++} + 2\,OH^- \rightleftharpoons Cu(OH)_2 \downarrow$$
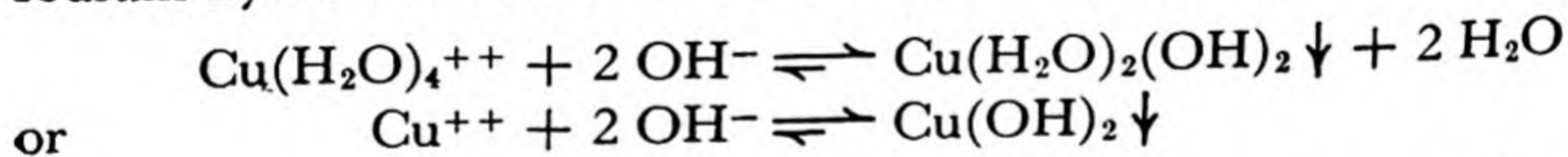
The hydroxide reacts with concentrated solutions of strong bases to form the dark blue cuprate ion.

$$Cu(H_2O)_2(OH)_2 \downarrow + 2\,OH^- \rightleftharpoons Cu(OH)_4^{--} + 2\,H_2O$$
or $$Cu(OH)_2 \downarrow + 2\,OH^- \rightleftharpoons Cu(OH)_4^{--}$$
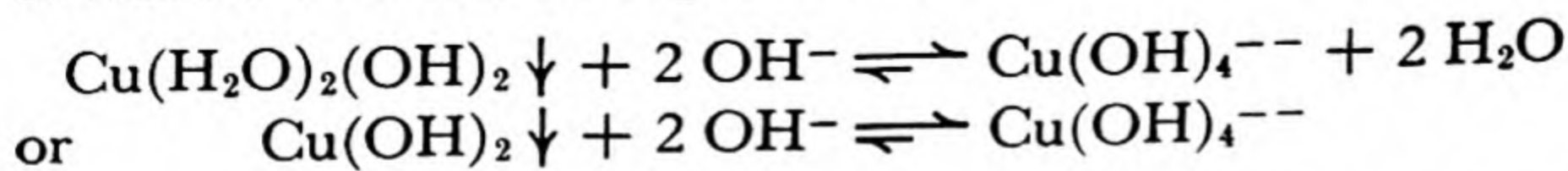
The hydroxide dissolves in an excess of ammonia to form the complex cupric ammonia ion, retaining the coordination number 4 in all of these compounds.

$$Cu(OH)_2 \downarrow + 4\,NH_3 \rightleftharpoons Cu(NH_3)_4^{++} + 2\,OH^-$$
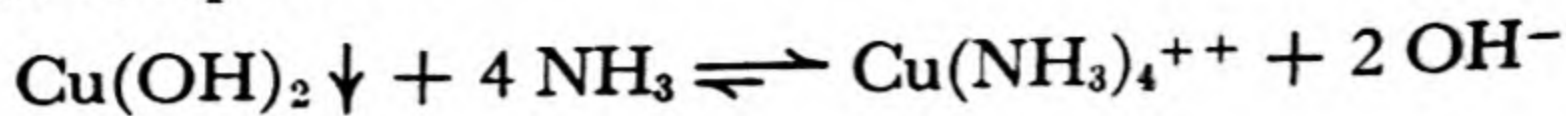
Cupric hydroxide is unstable, decomposing when heated — even in suspension in water — to form cupric oxide, a black solid.

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$
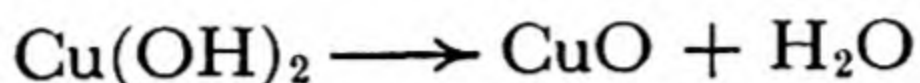
Furthermore, this oxide is formed by heating copper with an excess of air and by the thermal decomposition of the nitrate and carbonate.

$$2\,Cu(NO_3)_2 \longrightarrow 2\,CuO + 4\,NO_2 + O_2$$

Cuprous oxide, Cu_2O, is obtained by the mild reduction of cupric compounds in alkaline solution. This reaction is used in Fehling's test for the presence of dextrose and other reducing sugars. The reaction is an important diagnostic test for the presence of sugar in urine, as evidence of diabetes. A red precipitate of cuprous oxide is formed when an alkaline solution of cupric sulfate, containing a tartrate to form complex copper tartrate ions reducing the concentration of the cupric ions enough to prevent the precipitation of cupric hydroxide, is boiled in the presence of dextrose.

Chlorides of Copper. *Cupric chloride*, $CuCl_2$, may be obtained as a yellow anhydrous salt by the reaction of copper with chlorine.

$$Cu + Cl_2 \longrightarrow CuCl_2$$
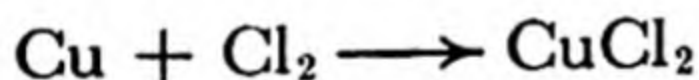
Cupric chloride may be prepared in solution by the reaction of hydrochloric acid with the oxide or carbonate.

$$CuO + 2\,H^+ \longrightarrow Cu^{++} + H_2O$$
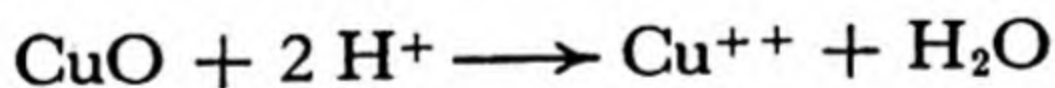
The hydrate, $CuCl_2(H_2O)_2$, a greenish blue solid may be crystallized from the solution. Dilute solutions of cupric chloride are blue because of the cupric ions. The more concentrated solutions have a green color because of the presence of the complex $CuCl_4^{--}$ ion in equilibrium with cupric ions:

$$Cu^{++} + 4\,Cl^- \rightleftharpoons CuCl_4^{--}$$
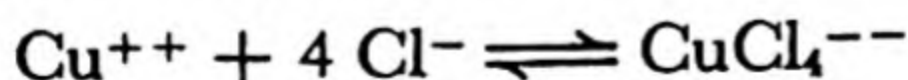
Cuprous chloride, $CuCl$, may be formed by boiling an acidic solution of cupric chloride with copper. The complex $CuCl_2^-$ ion is formed in concentrated solutions, but it decomposes to form a white precipitate of cuprous chloride when the solution is diluted.

$$Cu^{++} + Cu + 4\,Cl^- \longrightarrow 2\,CuCl_2^-$$
$$CuCl_2^- \rightleftharpoons CuCl \downarrow + Cl^-$$
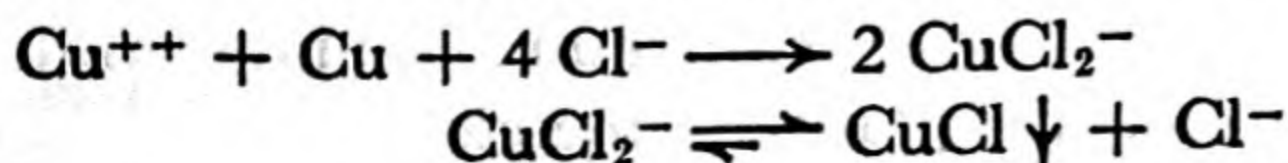
Cupric Nitrate. $Cu(NO_3)_2$. This salt may be prepared by the reaction of nitric acid with copper or with cupric oxide.

$$8 H^+ + 2 NO_3^- + 3 Cu \longrightarrow 2 NO + 3 Cu^{++} + 4 H_2O$$
$$CuO + 2 H^+ \longrightarrow Cu^{++} + H_2O$$
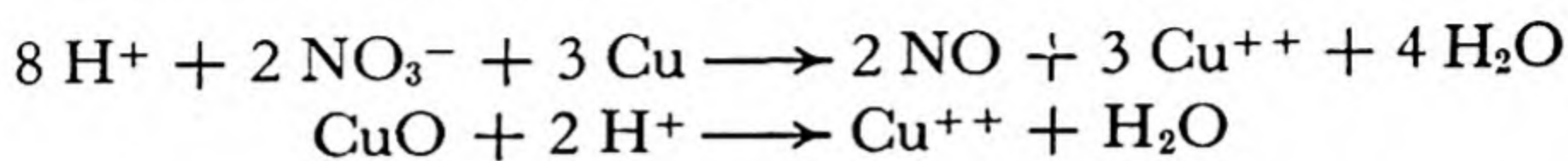
The salt crystallizes from solution as a blue hydrated solid, $Cu(NO_3)_2(H_2O)_6$. It is so soluble that it deliquesces when exposed to air under ordinary conditions of humidity. It is a convenient reagent for supplying cupric ions.

Cupric Sulfate. $CuSO_4$. Cupric sulfate is the most familiar and important of the cupric salts. It is prepared commercially by roasting copper sulfide ores to form a mixture of the oxide and sulfate.

$$Cu_2S + 2 O_2 \longrightarrow 2 CuO + SO_2$$
$$2 Cu_2S + 5 O_2 \longrightarrow 2 CuSO_4 + 2 CuO$$
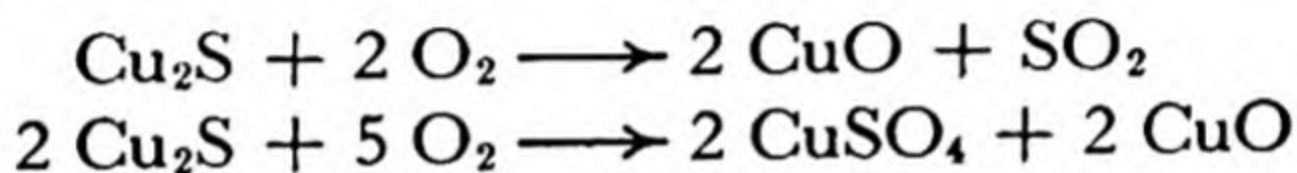
These products are dissolved in dilute sulfuric acid and cupric sulfate may be crystallized from the resulting solution. It may also be prepared by the reaction of copper with silver sulfate solutions.

$$Cu + 2 Ag^+ \longrightarrow Cu^{++} + 2 Ag$$
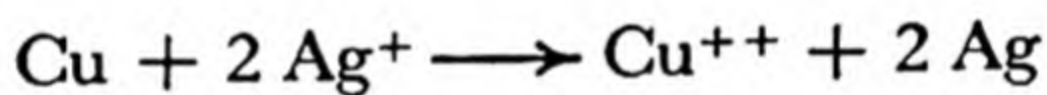
Cupric sulfate crystallizes from solution as the pentahydrate, $CuSO_4(H_2O)_5$, called *blue vitriol*. The anhydrous salt is white. Cupric sulfate is used in copper plating, in the electrorefining of copper, and as a mordant in dyeing. A small proportion of cupric sulfate may be added to water in reservoirs to prevent the growth of algae. Cupric salts in high concentrations are poisonous. *Bordeaux mixture* containing cupric hydroxysulfate mixed with calcium sulfate is prepared by the reaction of cupric sulfate with calcium hydroxide. The composition of this product is variable. It is used as a fungicide, especially on fruit trees and vines.

THE NOBLE METALS

Silver and gold have long been known as the noble metals. The three elements in Group VIII–B, immediately preceding each of these metals, resemble silver and gold in activity. These six elements, ruthenium, rhodium, palladium, osmium, iridium, and platinum, are known as the platinum metals.

Occurrence and Production of Silver. The metal occurs in native ores, usually associated with gold and with copper, and in sulfide ores frequently with lead sulfide. It also occurs as a chloride and in other minerals. More than one half of the annual production of silver is a by-product of copper and lead refining. Most of the silver in ores of copper and of lead remains in the crude metal. The extraction of silver from lead through the use of zinc in the Parkes process is discussed on page 476. Silver is separated from anode muds, obtained during the electrorefining of copper and lead, by treatment with dilute sulfuric acid, which dissolves the more active metallic ingredients, followed by fusion with silica and sodium carbonate. Silver produced in this manner contains whatever gold may have been present in the anode mud.

The cyanide process is used extensively for the extraction of silver from ores. Silver and its compounds may be dissolved by leaching the ore with dilute solutions of sodium cyanide. The reactions take place slowly and several days may be required to complete the extraction. The crushed ore is treated with the leaching solution, containing 0.25–0.7 per cent of sodium cyanide, in large tanks provided with stirrers to keep the materials mixed thoroughly. Air is blown through the suspension because oxidation is required in the extraction of the metal from native ores and from sulfide ores.

$$4\,Ag + 8\,CN^- + O_2 + 2\,H_2O \longrightarrow 4\,Ag(CN)_2^- + 4\,OH^-$$
$$Ag_2S + 4\,CN^- \rightleftharpoons 2\,Ag(CN)_2^- + S^{--}$$
$$2\,S^{--} + O_2 + 2\,H_2O \longrightarrow 2\,S + 4\,OH^-$$
$$AgCl + 2\,CN^- \longrightarrow Ag(CN)_2^- + Cl^-$$
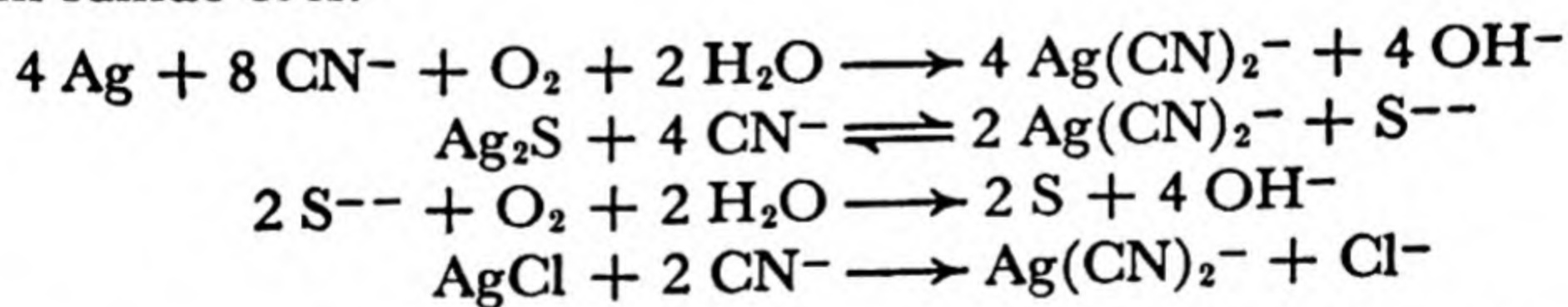
Silver is precipitated from the cyanide solution by the action of zinc dust.
$$2\,Ag(CN)_2^- + Zn \longrightarrow 2\,Ag + Zn(CN)_4^{--}$$
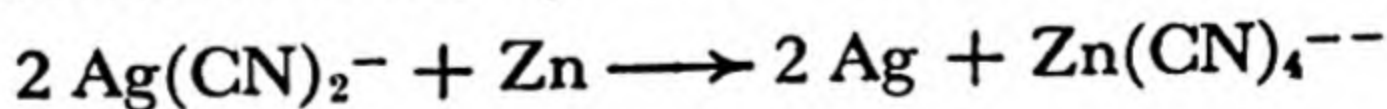
The amalgamation process is also employed for the separation of silver from the native ore and from the chloride ore. Free silver forms an amalgam with mercury, and the chloride ore is reduced to form free silver which also produces an amalgam.

$$2\,AgCl + 2\,Hg \longrightarrow Hg_2Cl_2 + 2\,Ag$$
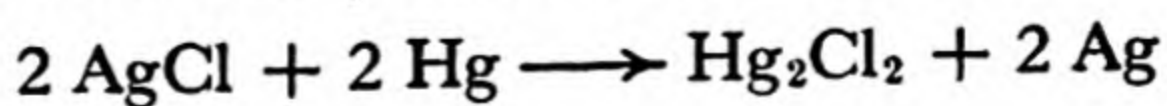
The amalgam is heated to distill out the mercury that may be used repeatedly.

The crude metal produced by these processes may be refined electrolytically by making it the anode in an electrolyte of silver nitrate. During the process, silver is dissolved at the anode and deposited at the cathode. Metals more active than silver, *e.g.*, copper, are also dissolved at the anode but are not deposited at the cathode. Less active metals, such as gold, are not dissolved but collect as a slime in cloth bags about the anodes.

Properties and Reactions of Silver. Some of the properties of the metal are listed in Table 39, page 483. Silver is a white metal with high luster and is very ductile and malleable. It is a better conductor of heat and electricity than any of the other metals. Silver is oxidized by ozone but under ordinary conditions does not react directly with oxygen. It reacts readily with sulfur and with hydrogen sulfide in air, causing tarnish.

$$2\,Ag + S \longrightarrow Ag_2S$$
$$4\,Ag + 2\,H_2S + O_2 \longrightarrow 2\,Ag_2S + 2\,H_2O$$
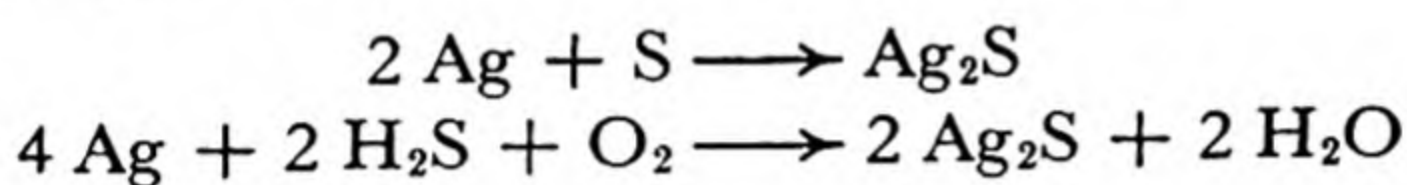
Silver is oxidized by nitric acid to form silver nitrate and by hot concentrated sulfuric acid to form the sulfate.

$$2\,H_2SO_4 + 2\,\epsilon \longrightarrow SO_2 + 2\,H_2O + SO_4^{--}$$
$$[Ag \longrightarrow Ag^+ + 1\,\epsilon] \times 2$$
$$\overline{2\,H_2SO_4 + 2\,Ag \longrightarrow SO_2 + 2\,Ag^+ + SO_4^{--} + 2\,H_2O}$$
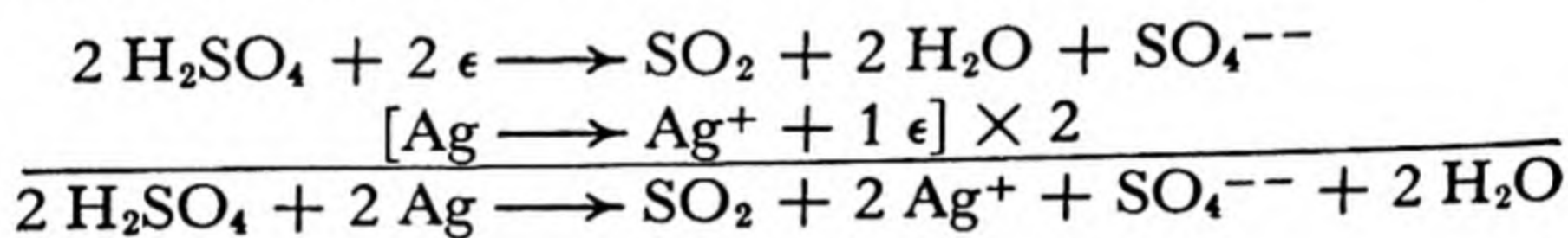
Uses of Silver. Silver is used as an ornamental metal for tableware and in coins. Pure silver is too soft for many applications and an alloy of silver and copper is commonly used. American silver coins contain 90 per cent of silver and sterling silver 92.5 per cent. Silver is used extensively in plating articles made of cheaper metals. The article to be plated is made the cathode with an electrolyte of potassium silver cyanide solution and anodes of pure silver bars. Silver is deposited more slowly and evenly from this electrolyte than from a solution of silver nitrate. Mirrors may be silvered by reducing an ammoniacal solution of silver nitrate with glucose or formaldehyde in contact with the thoroughly cleaned glass. The deposited film of silver is washed, dried, and varnished to protect it. Silver is used extensively in the preparation of its salts.

Compounds of Silver. Silver yields the simple ion, Ag^+, and the nitrate is its most familiar and important soluble salt. There are

several complex ions of silver, *e.g.*, silver ammonia ion, $Ag(NH_3)_2{}^+$; silver thiosulfate ion, $Ag(S_2O_3)_2{}^{---}$, and silver cyanide ion, $Ag(CN)_2{}^-$. The sulfate has moderate solubility and the halides and the sulfide are only slightly soluble.

Silver Oxide. Ag_2O. The direct union of silver with oxygen under a pressure of about 15 atmospheres at a temperature of 300° yields silver oxide. The oxide is precipitated by the reaction of silver nitrate with sodium hydroxide. Silver hydroxide is not stable at room temperature.

$$Ag^+ + 2\,OH^- \rightleftharpoons Ag_2O \downarrow + H_2O$$
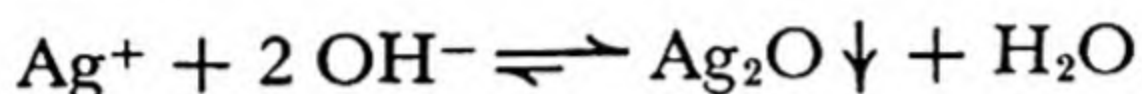
A suspension of the oxide in water contains a sufficiently high concentration of hydroxide ions to exhibit distinctly basic properties.

Silver Nitrate. $AgNO_3$. Silver nitrate is commonly prepared by the reaction of silver with nitric acid.

$$4\,H_3O^+ + NO_3{}^- + 3\,Ag \longrightarrow NO + 3\,Ag^+ + 6\,H_2O$$
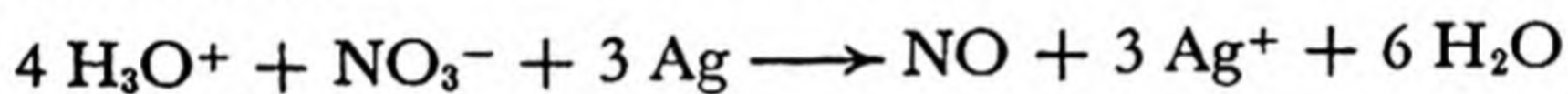
The solid melts at 212°. Silver nitrate is used in the preparation of germicidal solutions, and thin sticks of the solid are used in surgery as a cauterizing agent. It is an active oxidizing agent, reduced to elementary silver by some varieties of organic matter, so that it causes a stain on the hands and clothing. It is used in some indelible inks. Solutions of silver nitrate are the common laboratory sources of silver ions. Large quantities of this salt are required industrially for the preparation of silver halide emulsions for use in photography.

Silver Halides. These salts are precipitated by the reaction of solutions of silver nitrate with chloride, bromide, or iodide ions. Silver chloride is white, the bromide pale yellow, and the iodide distinctly yellow. Silver chloride dissolves readily in solutions of ammonia, because the formation of the silver ammonia complex ion reduces the concentration of silver ions below the required value for equilibrium with the solid.

$$AgCl \downarrow \rightleftharpoons Ag^+ + Cl^-$$
$$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2{}^+$$
$$[Ag^+] \times [Cl^-] < S_{AgCl}$$
$$AgCl \downarrow + 2\,NH_3 \longrightarrow Ag(NH_3)_2{}^+ + Cl^-$$
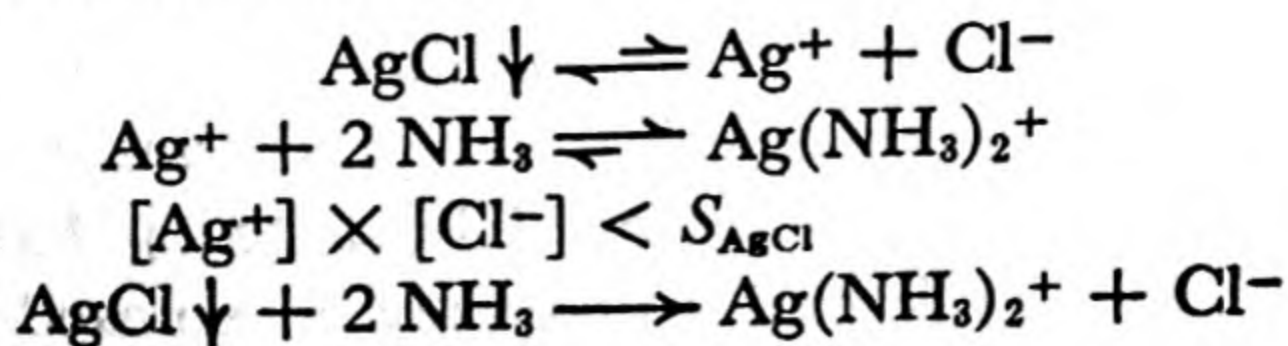
Silver bromide dissolves in solutions containing high concentrations of ammonia, but silver iodide does not furnish a high enough concentration of silver ions to lead to the reaction with ammonia. All three of the slightly soluble silver halides dissolve readily in cyanide solutions and in solutions of sodium thiosulfate.

$$AgBr \downarrow + 2\,CN^- \longrightarrow Ag(CN)_2^- + Br^-$$
$$AgI \downarrow + 2\,S_2O_3^{--} \longrightarrow Ag(S_2O_3)_2^{---} + I^-$$
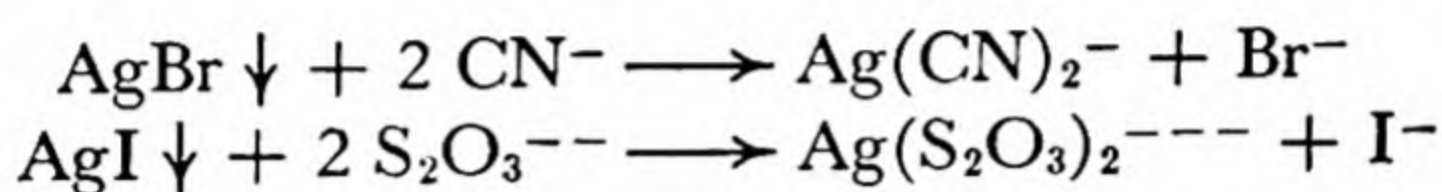
Photography. Silver halides darken when exposed to white light. This is due to the decomposition of the salts with the formation of elementary silver. Decomposition occurs more rapidly under the action of X-rays and ultraviolet light than of visible light. Silver bromide is the most sensitive of these salts to the action of light, and because of this property, it is used extensively in photography.

The sensitized film or plate is prepared by coating a transparent film of cellulose nitrate or cellulose acetate, or a glass plate, with a gelatin emulsion containing the finely dispersed, light-sensitive, silver bromide. The emulsion is then allowed to harden. It must be protected from white light until the exposure is made in the camera. The required time of exposure depends on the intensity of the light and the sensitivity of the emulsion. The sensitivity of emulsions is increased by traces of sulfur compounds. The silver salt is partially decomposed during the exposure, with the formation of minute particles of uncombined silver. The incipient decomposition is greatest where the most intense light strikes the film. No visible change in the appearance of the film is caused during the exposure. The exposed film is developed by immersing it for the proper length of time in a solution of a mild reducing agent, such as pyrogallol or an alkaline solution of hydroquinone. The rate of reduction is greatest in the part of the film where the incipient change, caused by the exposure to the most intense light, was greatest. Therefore, the thickness of the deposit of metallic silver formed on the film during the developing process depends on the intensity of the light that fell on the film during the brief time of the exposure. When the reaction has proceeded far enough, the unchanged silver salts are removed by a fixing bath, a solution of sodium thiosulfate. The film may now be exposed to white light

without harmful result. The film is washed and dried after the completion of the fixing. The developed film is known as a negative, because the light and dark parts of the image are opposite to those on the object photographed.

A print is produced by placing the negative over sensitized printing paper and making an exposure to light for the proper length of time. The printing paper is coated with an emulsion similar to that on the film, but less sensitive. The exposed print is developed, fixed, and washed as in the treatment of the film. Light and dark parts are again reversed producing a positive.

Gold. Gold occurs in the free condition frequently alloyed with other metals such as copper, lead, and silver. It also occurs in combination with tellurium in some of the sulfide ores of copper and lead. It is not abundant but is widely distributed. It occurs in veins in quartz and in alluvial sands. The sands are agitated with water in placer mining, and particles of gold settle while sand is washed away. Gold in quartz veins may be separated by crushing the ore and washing the pulverized material over amalgamated copper plates. The larger particles of gold settle and are amalgamated with the mercury. The amalgam is removed and distilled, leaving gold as a residue. The more finely divided particles, which escape amalgamation, are dissolved as in the leaching of silver ores by solutions of sodium cyanide, forming the complex cyanide.

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O \longrightarrow 4\,Au(CN)_2^- + 4\,OH^-$$
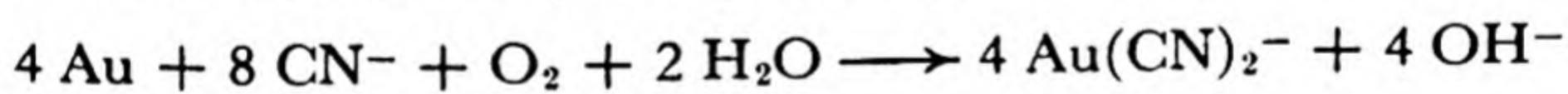
Gold is displaced from this solution by zinc.

$$Zn + 2\,Au(CN)_2^- \longrightarrow 2\,Au + Zn(CN)_4^{--}$$
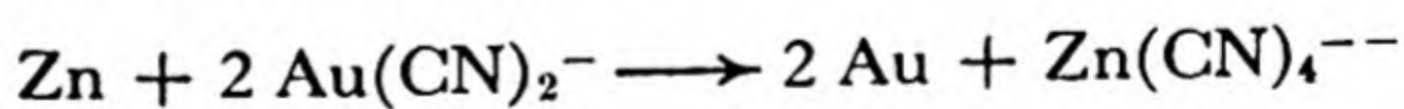
Gold possesses a familiar, yellow luster and is the most malleable and ductile of the metals. Some of its properties are listed in Table 39, page 483. Gold is alloyed, usually with copper, for use in jewelry. White gold may be produced by alloying the metal with nickel and zinc. The purity of gold is expressed in carats fine. Pure gold is 24 carats fine, and good jewelry usually is 14–18 carats fine. A thin coating of gold is often deposited on copper in producing cheap jewelry. This may be done by an electroplating process from a solution of the complex aurocyanide. Gold with a fixed value of \$20.67 per troy ounce was the basis of the monetary system

of the United States for many years. The legal price of gold was fixed at $35 an ounce in 1934.

Reactions of Gold. Gold is the least active of the metals. It does not combine with oxygen or with sulfur and does not react with any of the familiar acids. It does, however, combine with chlorine and bromine and react with acidic solutions containing free chlorine, bromine, or iodine. It is slowly attacked by fused nitrates and alkali metal hydroxides, forming aurates, e.g., $KAuO_2$. The reaction with cyanides has been mentioned in connection with leaching the metal from its ores. Solutions of gold salts are usually prepared by the reaction of the metal with aqua regia, forming chlorauric acid, $HAuCl_4$.

$$4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow NO + 2\,H_2O$$
$$Au + 4\,Cl^- \longrightarrow AuCl_4^- + 3\,\epsilon$$
$$\overline{4\,H^+ + NO_3^- + Au + 4\,Cl^- \longrightarrow NO + AuCl_4^- + 2\,H_2O}$$
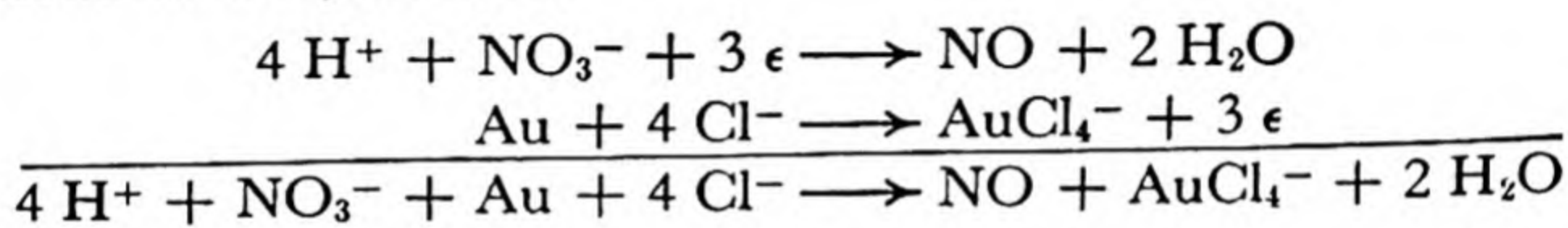
Compounds of Gold. Gold yields compounds in the oxidation states $1+$ and $3+$. Crystalline chlorauric acid, $HAuCl_4(H_2O)_3$, may be separated from concentrated solutions. This acid reacts with sodium hydroxide, with the formation of sodium chloraurate. The acid decomposes when heated gently, forming hydrogen chloride and auric chloride.

$$HAuCl_4 \rightleftharpoons HCl + AuCl_3$$
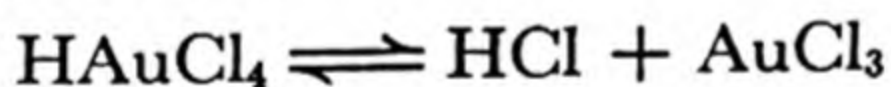
Auric chloride decomposes at 170–180° into aurous chloride and chlorine.

$$AuCl_3 \rightleftharpoons AuCl + Cl_2$$
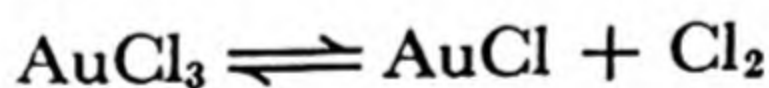
This compound decomposes in hot water with the formation of the uncombined metal and auric chloride.

$$3\,AuCl \longrightarrow AuCl_3 + 2\,Au$$

The Platinum Metals. The metals of the second and third triads in Group VIII-B of the periodic system are *ruthenium, rhodium,* and *palladium* and *osmium, iridium,* and *platinum,* respectively. They yield compounds in more than one oxidation state and are easily reduced from their compounds. They have high melting points, ranging from 1755° for palladium to 2700° for osmium. The specific gravities of the metals in the first triad are about 12, ruthenium 12.06, rhodium 12.1, and palladium

11.97, but are much greater in the second triad, osmium 22.48, iridium 22.42, and platinum 21.45. The metals occur in the native condition, alloyed with each other and with other metals of low activity, such as copper and gold. The nickel arsenide ore of Ontario is now the leading source of these metals. The platinum metals are also obtained from Russia, South Africa, the United States, and Colombia.

The first step in the production of the metals from placer deposits is concentration by washing. A crude metal containing 60–85 per cent of platinum metals may be obtained in this manner. Platinum and several of the other metals are dissolved from the concentrates by reaction with warm aqua regia, leaving an alloy of osmium and iridium as a residue. The solution and the residue are then treated by chemical methods to produce the separate metals or their alloys.

Platinum is the most important of these metals. It has a high degree of ductility and malleability, a high melting point, 1773°, and low chemical activity. It is extensively used in making wire, foil, crucibles, and other forms of laboratory ware. It is attacked by fused alkali metal hydroxides, with the formation of platinates, such as K_2PtO_3, and by aqua regia with the formation of chloroplatinic acid, H_2PtCl_6. Platinum forms alloys with several metals in addition to the other platinum metals, gold and silver, *e.g.*, lead, tin, bismuth, and mercury. It also reacts slowly with some of the nonmetals, *e.g.*, carbon, phosphorus, sulfur, and arsenic. Hence, these substances damage platinum apparatus if they are brought in contact with the heated metal. Platinum is an important contact catalyst in chemical industry, *e.g.*, in the contact process for the production of sulfuric acid and in the production of nitric acid from ammonia. Platinum also has important uses in the electrical industry in magneto contacts, relays, thermoammeters, and in voltage regulators. Its uses in dentistry include bridges, braces, and other orthodontic appliances. The most extensive use of the metal, however, is in jewelry.

EXERCISES

1. Discuss the structural relationships between the atoms of the elements of Group I-B and those of Group I.

2. Describe the production of copper from sulfide ores and from oxidized ores.
3. What procedures are employed for the extraction of copper from low grade ores?
4. Describe the electrolytic refining of copper, showing how it provides for the elimination of the different classes of impurities likely to be present in crude copper.
5. What two simple ions does copper yield? Write equations for reactions which illustrate the formation of each from the other.
6. In terms of theory, account for the formation of a number of complex ions of copper. Explain how the formation of these complex ions may be applied to cause the solution of copper compounds of low solubility.
7. Describe methods that may be used for the production of silver from its ores.
8. Represent by equations the reactions — if any — of copper, silver, and gold with oxygen, sulfur, chlorine, and acids.
9. Indicate by equations the reactions involved in the production of the following compounds: (a) cupric sulfate; (b) cupric chloride; (c) silver nitrate; (d) chlorauric acid; (e) chloroplatinic acid.
10. Discuss the use of silver salts in photography.

SUPPLEMENTARY READINGS

Hayward, C. R., *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1929, chaps. I, XIV, XV, XVI.

Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940, chaps. VII, XX.

Mees, C. E. K., *Photography*, The Macmillan Company, New York, 1937.

Lee, J. A., "Silver, Gold, Tantalum, and the Platinum Metals," *Ind. Eng. Chem.* **28,** 1412 (1936).

"Copper," *Fortune*, **XIV**, 6, 83 (1936).

"Silver," *Fortune*, **XII**, 1, 74 (1935).

"Gold," *Fortune*, **XIII**, 2, 69 (1936).

Chapter 31

ZINC. CADMIUM. MERCURY

Zinc, cadmium, and *mercury* are the metals of Group II–B of the periodic system. The atoms of these metals contain two valence electrons and differ from the atoms of the metals of Group II in that the outer shell of the atomic kernel contains eighteen electrons, whereas the number in the corresponding shell of atoms of the alkaline earth metals is eight. Zinc, cadmium, and mercury are less active than the metals of Group II, and their hydroxides are less soluble and also less actively basic. The activity of the metals in this group decreases in the order of their atomic numbers, so that mercury is the least active metal in the group. These metals yield simple divalent positive ions and a number of complex ions.

ZINC AND CADMIUM

Zinc ores are found widely distributed in the United States. The most important ore of zinc is the sulfide ore containing the mineral *sphalerite,* ZnS, known also as zinc blende. In the Missouri, Kansas, and Oklahoma deposits, the sulfide is associated with galena, lead sulfide. Sphalerite ores are found in Montana and some of the other states. Zinc carbonate ore, containing the mineral *smithsonite,* $ZnCO_3$, is found in Arkansas and Colorado. *Zincite,* ZnO, and *franklinite,* $ZnOFe_2O_3$, are found in zinc ores in New Jersey. These ores are complex and contain only small percentages of zinc, often less than 5 per cent. Cadmium occurs as the sulfide, CdS, in the mineral *greenockite.* Cadmium compounds are present in small proportions in many of the ores, particularly in zinc ores.

Production of Zinc. Two processes are in general use for the production of zinc from its ores. In the retort process, zinc oxide is reduced by carbon in clay retorts. In the electrolytic process, the roasted ore is leached to produce a solution of zinc sulfate

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which is then electrolyzed. The retort process is the more extensively used, while the electrolytic process offers certain advantages in the production of pure zinc and in the recovery of other metals from the ores, *e.g.*, lead, copper, cadmium, and the noble metals.

The Retort Process. This process is applicable to the three main classes of zinc ores, *viz.*, the oxide ores, the carbonate ores, and the sulfide ores. The steps in the process are indicated in outline in
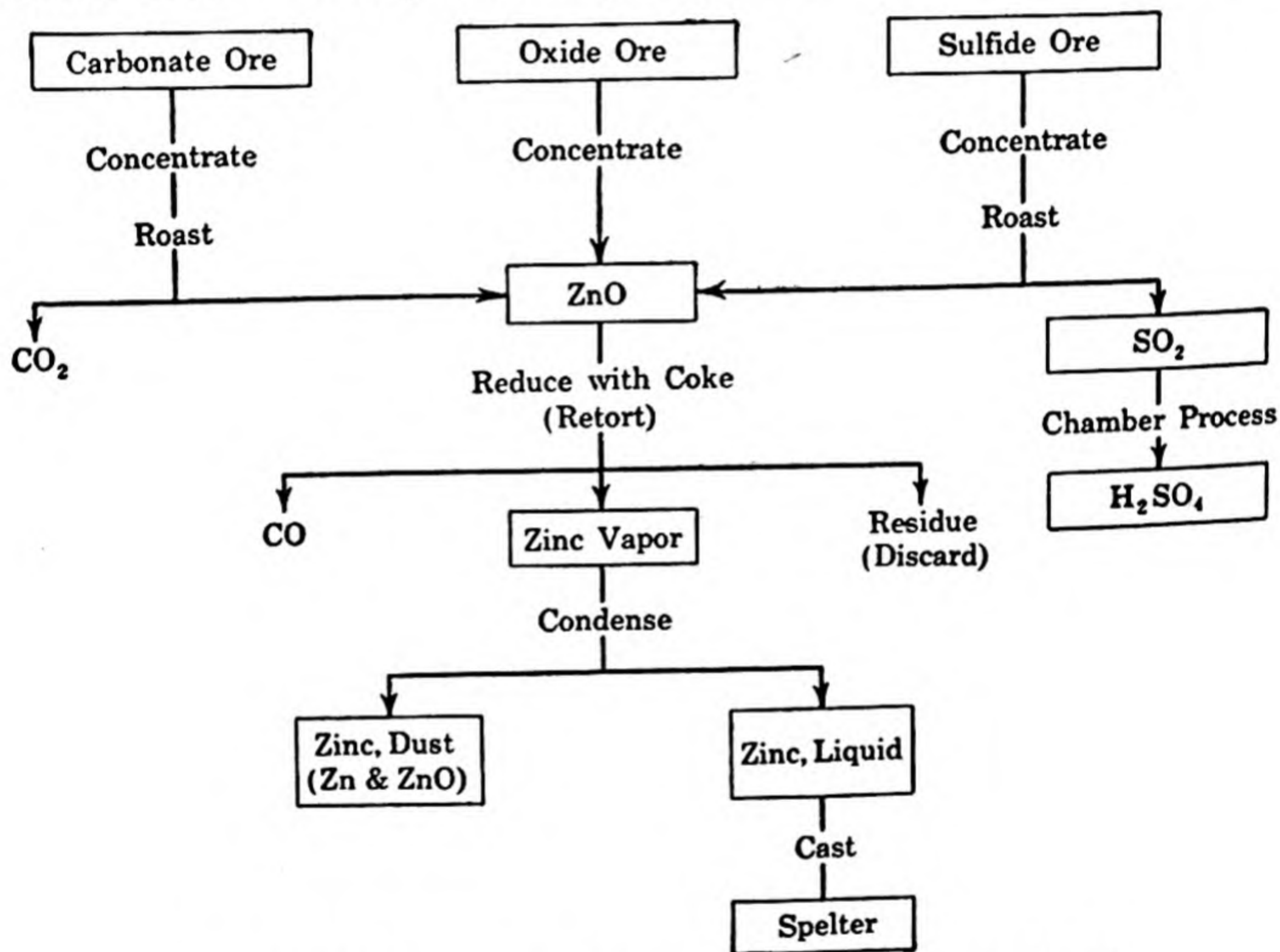
Fig. 126. Outline — Production of Zinc by the Retort Process

Fig. 126. The ores are concentrated by washing and by oil flotation. The carbonate is decomposed by heat, with the formation of oxide and carbon dioxide.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
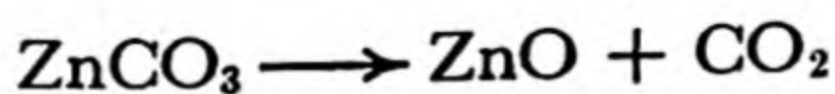
The sulfide ores are roasted to form the oxide and sulfur dioxide.

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$
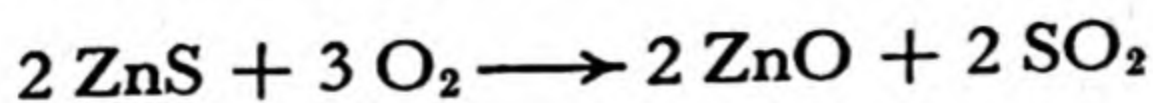
Sulfuric acid produced from sulfur dioxide is an important by-product of the process. A mixture of zinc oxide with an excess of

coke or coal is heated in a tube-shaped retort made of fire clay at a temperature of approximately 1200°.

$$ZnO + C \longrightarrow Zn + CO$$
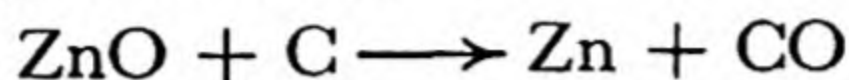
The boiling point of zinc is 907°. Consequently, the metal is distilled from the retorts and condensed in the receivers. A finely
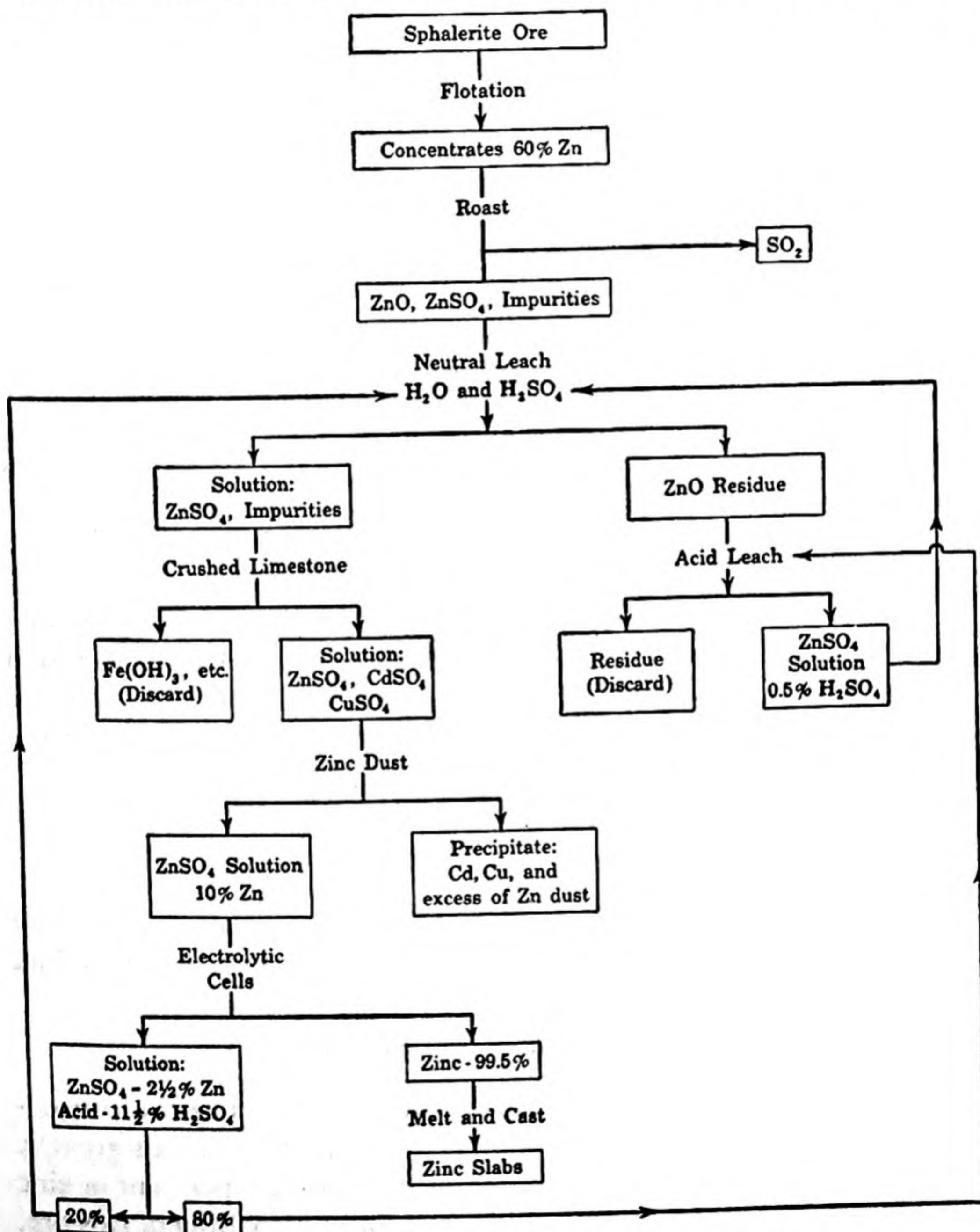
Fig. 127. Outline — Production of Zinc by the Electrolytic Process

divided solid, called *zinc dust*, is formed by the condensation of the vapors when the receivers are cold. This product contains about 10 per cent of zinc oxide. Some of the zinc dust is swept out of the receivers by carbon monoxide and is not recovered. Usually, the temperature of the receiver is maintained above the melting point of zinc, 419.4°, but below 500° to avoid too great loss of vapor. The metal is cast into slabs weighing about 65 lb. This product is known as *spelter*. The metal produced in this manner contains small percentages of impurities such as lead and cadmium. It may be further purified by redistillation.

The Electrolytic Process. An outline of the steps in the production of zinc by this process is shown in Fig. 127. The concentrated sulfide ore is roasted at a lower temperature than in the retort process, and a mixture of the oxide and sulfate is produced.

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$
$$ZnS + 2\,O_2 \longrightarrow ZnSO_4$$
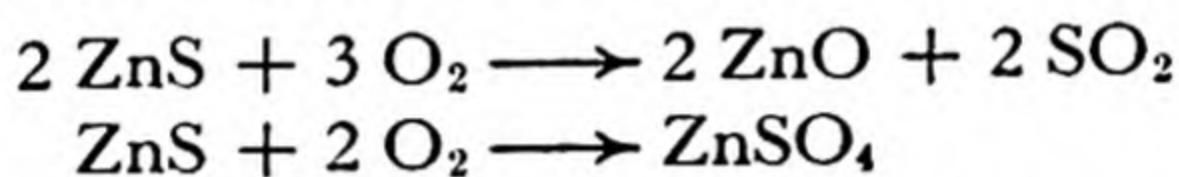
The sulfate and oxide are leached from the roasted product by the acidic solution from the electrolytic cells.

$$ZnO + 2\,H^+ \longrightarrow Zn^{++} + H_2O$$
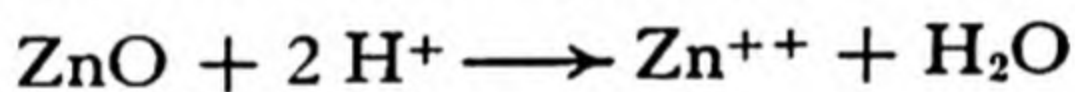
Crushed limestone is added to the solution from the leaching operations to neutralize any free acid, and to cause the precipitation of compounds of iron, antimony, and arsenic. To displace copper and cadmium, zinc dust is added to the clear solution after the removal of the precipitate containing iron.

$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$$
$$Zn + Cd^{++} \longrightarrow Zn^{++} + Cd$$
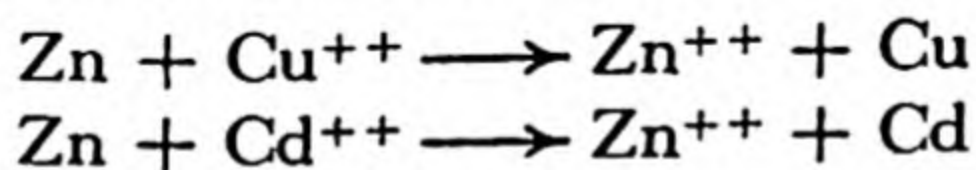
The solution is now electrolyzed with the deposition of zinc at the cathode and the regeneration of sulfuric acid by the anode reaction.

$$[Zn^{++} + 2\,\epsilon \longrightarrow Zn] \times 2$$
$$4\,OH^- \longrightarrow 2\,H_2O + O_2 + 4\,\epsilon$$
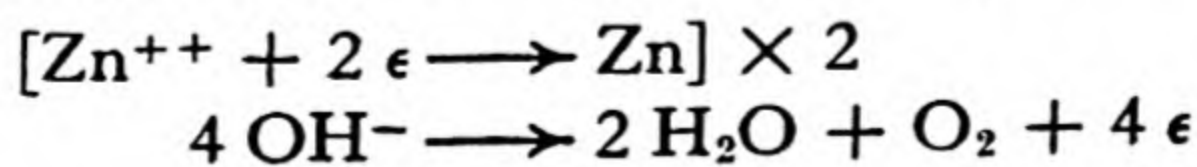
The current efficiency in depositing zinc decreases as the concentration of zinc ions becomes smaller and of hydrogen ions greater. Consequently, the electrolyte containing about 2.5 per cent of zinc and 11.5 per cent of sulfuric acid is used for the leaching of raw ore, without attempting to deposit all of the zinc it contains.

Production of Cadmium. Cadmium is obtained as a by-product in the production of other metals, such as zinc, lead, and copper. In the retort process for zinc, cadmium collects in the first portions of distilled zinc, because it has a lower boiling point (767°) than zinc (907°), and its oxide is reduced the more readily. This portion may be redistilled to effect further separation of cadmium from zinc. The metal may also be produced from dusts deposited in flues of the furnaces in which zinc, lead, and copper ores are roasted. The dusts are treated with sulfuric acid, and cadmium is then deposited by displacement with zinc. The principal source of cadmium, however, is the mixture of metals displaced by zinc dust in the final purification of the zinc sulfate solutions for electrolysis. This precipitate contains copper, cadmium, the excess of zinc, and other metals. It is roasted at low temperature and dissolved in sulfuric acid. Just enough zinc dust is now added to displace copper, and the cadmium is then deposited by passing the solution through scrap zinc. The spongy metal formed in this way may be redissolved in sulfuric acid, and the solution electrolyzed to form metallic cadmium in a purity of 99.95 per cent.

Properties and Reactions of Zinc and Cadmium. Some of the physical properties of these metals are listed in Table 41, along with corresponding properties of mercury.

TABLE 41. PROPERTIES OF ZINC, CADMIUM, AND MERCURY

Property	Zinc	Cadmium	Mercury
Atomic weight	65.38	112.41	200.61
Atomic number	30	48	80
Isotopes	64, 66, 67, 68, 70	106, 108, 110, 111, 112, 113, 114, 116	196, 197, 198, 199 200, 201, 202, 204
Electron structure	2, 8, 18, 2	2, 8, 18, 18, 2	2, 8, 18, 32, 18, 2
Oxidation numbers	2 +	2 +	1 +, 2 +
Melting point (° C.)	419.40	320.90	− 38.87
Boiling point (° C.)	907.0	767.0	356.9
Density at 20°, g. per ml.	7.140	8.640	13.546

Zinc is a silvery white metal, brittle when cast but sufficiently malleable and ductile at 100–150° to be rolled into sheet and drawn into wire. Cadmium is also a silvery white metal. It is softer than zinc and is malleable and ductile. It may be rolled into foil and drawn into wire. Both zinc and cadmium form alloys with a number of metals.

Zinc and cadmium combine readily with oxygen and with other nonmetals.

$$2\,Zn + O_2 \longrightarrow 2\,ZnO$$
$$Cd + Cl_2 \longrightarrow CdCl_2$$
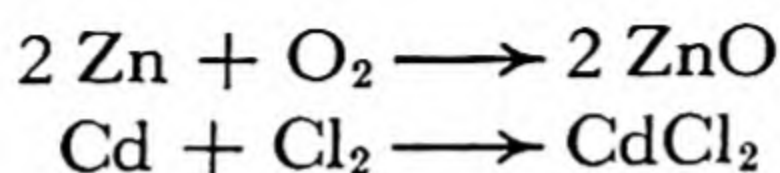
They also displace hydrogen from acids and ions of less active metals from solutions of their salts.

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$$
$$Cd + Cu^{++} \longrightarrow Cd^{++} + Cu$$
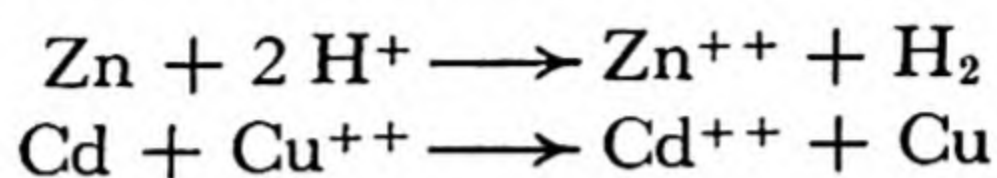
Cadmium is less active than zinc in all of these reactions. Both of these metals react slowly with oxygen at ordinary temperatures, but the surface of the metal becomes coated with an adherent film of the oxide and hydroxycarbonate in contact with moist air. Consequently, the metals are protected by this coating and do not corrode easily.

Uses of Zinc and Cadmium. Zinc and cadmium are used widely to protect iron and steel from rust. The surface of the metal to be coated must be first cleaned in dilute sulfuric acid to remove the surface oxide which would cause the protective metal coating to peel off. *Galvanized iron* is then made by dipping the iron into a bath of melted zinc. *Sherardized iron* is formed by baking the cleaned metal with zinc dust in closed drums. Zinc forms an alloy with the surface layer of iron, and the coating does not scale off so easily as in galvanized iron. The zinc coating may also be deposited electrolytically. The cadmium coating is commonly deposited by electrolysis and the articles are then heat-treated to cause the cadmium to alloy with iron.

Zinc is used as the active metal in dry cells, for the extraction of silver from lead, and for the precipitation of gold and silver from the complex cyanide solutions formed by leaching the ores of these metals. It is used in the manufacture of roofing shingles and gutters, because it does not corrode badly. Many alloys contain zinc. The most important zinc alloys are brass, an alloy of copper and zinc, and bronze, an alloy of copper, zinc, and tin. Cadmium is used in the production of alloys of low melting point and in the formation of antifriction alloys. One of the important uses of cadmium is in the production of bearing metals for internal combustion engines.

Metallic zinc is used in the preparation of some of its compounds, e.g., zinc oxide which finds widespread application in paint and in rubber. Cadmium yields a yellow sulfide which is used as a paint pigment.

Compounds of Zinc and Cadmium. Both zinc and cadmium yield ions having an electrovalence of 2 +. These ions are commonly represented by the symbols Zn^{++} and Cd^{++}, respectively, although some of their properties are more satisfactorily represented in terms of the formulas of the hydrated cations. The common soluble zinc salts are the chloride and sulfate. The nitrate is also soluble. Zinc ions are cation acids, hydrolyzing to form hydronium ions.

$$Zn(H_2O)_4{}^{++} + H_2O \rightleftharpoons Zn(H_2O)_3(OH)^+ + H_3O^+$$

or
$$Zn^{++} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$$
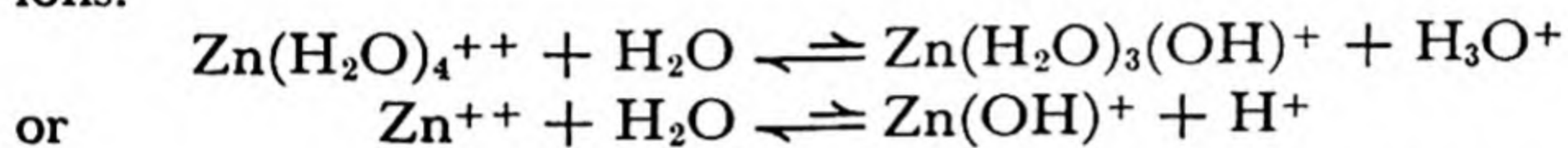
There are also a number of other complex ions of zinc, e.g., zinc hydroxide complex ion, $Zn(OH)_4{}^{--}$, zinc ammonia complex ion, $Zn(NH_3)_4{}^{++}$, and zinc cyanide complex ion, $Zn(CN)_4{}^{--}$.

Zinc Oxide. ZnO. Zinc oxide is prepared commercially by burning zinc vapor and by roasting zinc sulfide. It is a white powder that does not melt at the temperature of the oxyhydrogen blowpipe but becomes heated to incandescence. After such treatment it continues to glow for some time. Zinc oxide has many important uses, as a filler in rubber for automobile tires, in white paint and enamels, in the manufacture of oilcloth and linoleum, and in the preparation of zinc ointments and adhesive tape.

Zinc Hydroxide. $Zn(OH)_2$. This slightly soluble hydroxide is precipitated by the reaction of limited proportions of sodium hydroxide with a soluble zinc salt.

$$Zn^{++} + 2\,OH^- \rightleftharpoons Zn(OH)_2 \downarrow$$
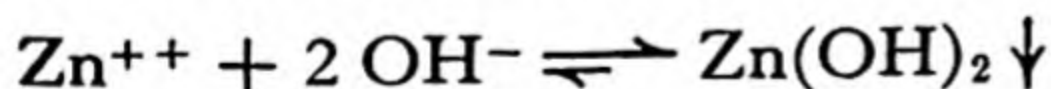
Since zinc hydroxide is an ampholyte, it reacts with an excess of the hydroxide and also with an excess of acids.

$$Zn(OH)_2 \downarrow + 2\,OH^- \longrightarrow Zn(OH)_4{}^{--}$$
$$Zn(OH)_2 \downarrow + 2\,H^+ \longrightarrow Zn^{++} + 2\,H_2O$$
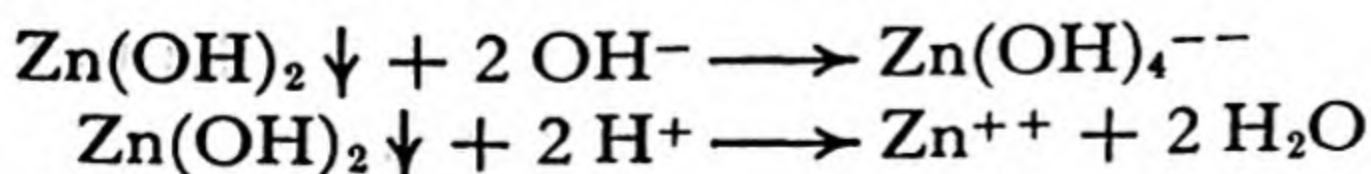
Zinc hydroxide also reacts with an excess of ammonia to form zinc ammonia complex ions.

$$Zn(OH)_2 \downarrow + 4\,NH_3 \longrightarrow Zn(NH_3)_4{}^{++} + 2\,OH^-$$
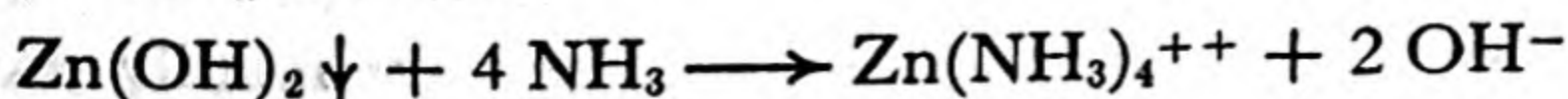
Zinc Chloride. ZnCl₂. This salt may be prepared by the direct union of zinc with chlorine and by the reaction of the metal or its oxide with hydrochloric acid. The hydrate, $ZnCl_2(H_2O)_2$, may be crystallized from solution. Zinc chloride is so soluble that the solid deliquesces in moist air. Concentrated solutions of zinc chloride convert cellulose into a gelatinous mass, which hardens as it dries, forming a product which is almost impervious to water. Because of this property it is used as a timber preservative and in the production of parchmentized paper. Zinc chloride is also used as an acid flux to remove oxides from metal surfaces in soldering.

Zinc Sulfate. ZnSO₄. Zinc sulfate is formed in solution by the reaction of the metal or its oxide with sulfuric acid. It crystallizes from solution as the heptahydrate, $ZnSO_4(H_2O)_7$, and is known as one of the vitriols. It may also be prepared by roasting zinc sulfide at moderate temperature with a free supply of air. Zinc sulfate is used in the laboratory as the common zinc salt. It is used commercially in the preparation of lithopone, a white pigment composed of barium sulfate and zinc sulfide. (See page 452.)

Slightly Soluble Zinc Salts. Salts of this type are commonly prepared by precipitation. *Zinc sulfide*, ZnS, is a white substance produced by the reaction of hydrogen sulfide in weakly acidic or in basic solutions of zinc salts.

$$Zn^{++} + H_2S + 2\,C_2H_3O_2^- \rightleftharpoons ZnS \downarrow + 2\,HC_2H_3O_2$$
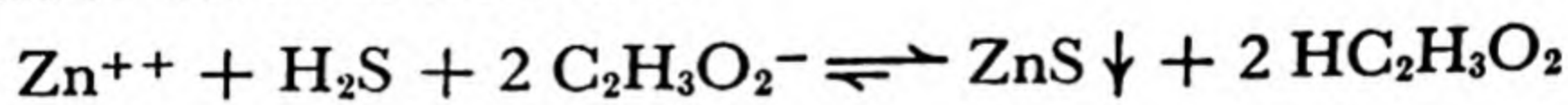
Zinc hydroxycarbonate, having inexact composition, possibly $Zn(OH)_2ZnCO_3$, is precipitated by the reaction of solutions of sodium carbonate with soluble zinc salts. The white crystalline *zinc ammonium phosphate*, $ZnNH_4PO_4$, may be precipitated by passing ammonia into acidic solutions containing zinc and hydrogen phosphate ions.

$$Zn^{++} + H_2PO_4^- + 2\,NH_3 \rightleftharpoons ZnNH_4PO_4 \downarrow + NH_4^+$$
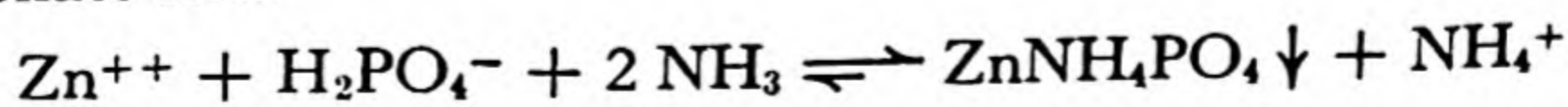
Soluble ferrocyanides react with solutions of zinc salts to form a white precipitate of *zinc ferrocyanide*, $Zn_2Fe(CN)_6$.

$$2\,Zn^{++} + Fe(CN)_6^{----} \rightleftharpoons Zn_2Fe(CN)_6 \downarrow$$
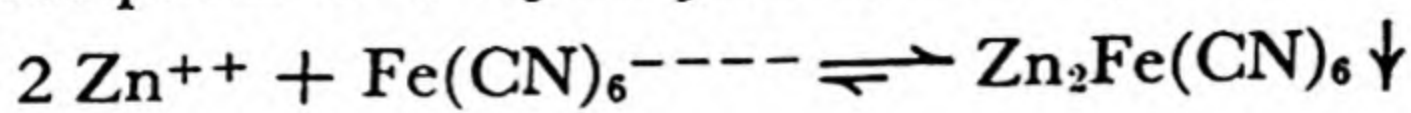
Compounds of Cadmium. The common soluble cadmium salts are the chloride, nitrate, and sulfate. They are readily prepared

by the reaction of the appropriate acid with the metal or its oxide. The cadmium ion hydrolyzes to form an acidic solution.

$$Cd^{++} + H_2O \rightleftharpoons CdOH^+ + H^+$$
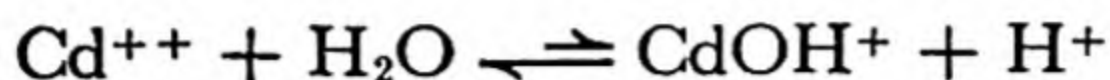
Among the slightly soluble compounds, which are easily prepared by precipitation, are the hydroxide, the carbonate, the phosphate, the sulfide, and the ferrocyanide. Cadmium hydroxide is more basic than zinc hydroxide and does not react with solutions of sodium hydroxide. Cadmium yields complex ions with ammonia, $Cd(NH_3)_4^{++}$, with cyanide, $Cd(CN)_4^{--}$, and with halides, CdI_4^{--}.

MERCURY

The resemblance of mercury to zinc and cadmium is not close, and the metal shows a greater similarity to copper and silver than to the other metals in Group II–B. The important ore of mercury is *cinnabar*, HgS. Italy, Spain, and the United States are normally the leading producers of this metal. The ore usually contains only about 0.5–1 per cent of mercury.

The Production of Mercury. Metallic mercury is obtained by heating the sulfide ore in air, with sulfur dioxide as a by-product.

$$HgS + O_2 \longrightarrow Hg + SO_2$$
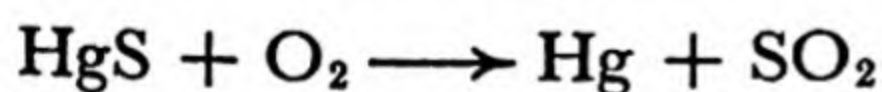
Mercury vapor is condensed from the gaseous products. Mercury may be purified by washing it with dilute nitric acid (Fig. 128),

Fig. 128. Purification of Mercury

which oxidizes the more active metallic impurities present, especially zinc and cadmium. Redistillation serves to effect further purification.

Properties and Reactions of Mercury. Some of the important physical properties of the metal are listed in Table 41, page 505. Mercury vapor is poisonous. Mercury does not react with oxygen

at ordinary temperatures and reacts only slowly at 300°. The oxide decomposes at temperatures above 400°. Mercury reacts readily with sulfur and with the halogens. The metal is below hydrogen in activity, but it reacts with nitric acid and with hot concentrated sulfuric acid, producing mercurous salts if an excess of mercury is used and mercuric salts with an excess of the acid.

Uses of Mercury. The use of mercury in thermometers is based on the fact that the metal is a liquid over the range representing the commonly observed temperatures, and that it has a fairly uniform coefficient of expansion. The high density and low vapor pressure of the liquid at ordinary temperatures make it suitable for use in barometers. Hot mercury vapor conducts electricity and gives out light that is rich in the ultraviolet rays. The common metals except iron and platinum form alloys with mercury, known as *amalgams*. This property finds application in the amalgamation process for the extraction of gold and silver from ores. Amalgams of tin, silver, and gold are used in dentistry. Limited use is made of mercury as a liquid in heat engines because of the high efficiency which these engines offer for the transfer of heat energy into work.

Compounds of Mercury. Mercury yields two series of compounds, *viz.*, *mercuric compounds* in which the metal has an oxidation number of 2 +, and *mercurous compounds* with an oxidation number of 1 +. The mercury atom contains two valence electrons. The mercurous ion contains two atoms in the form of the complex particle, $(Hg:Hg)^{++}$, which exists not only in solutions but also in solid compounds. This particle is so stable that mercurous ions do not readily form complex ions with other substances and require vigorous oxidation for conversion into mercuric ions. Mercurous ions are formed from mercuric ions by mild reduction.

$$Hg^{++} + Hg \longrightarrow Hg_2^{++}$$
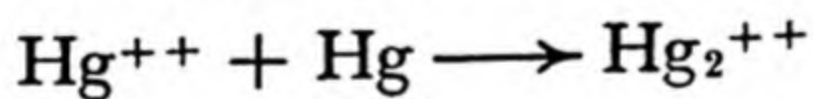
Both mercuric and mercurous ions hydrolyze to form acidic solutions and to yield precipitates of hydroxy salts, unless an excess of free acid is present in the solution.

Oxides of Mercury. *Mercurous oxide*, Hg_2O, is precipitated as a brownish-black solid by the reaction of sodium hydroxide with soluble mercurous salts.

$$Hg_2^{++} + 2\,OH^- \longrightarrow Hg_2O\downarrow + H_2O$$
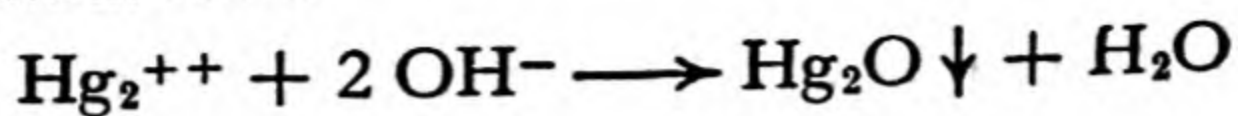
This oxide is unstable toward both heat and light, decomposing to form a mixture of free metal and mercuric oxide.

$$Hg_2O \longrightarrow Hg + HgO$$
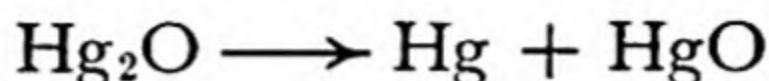
Mercuric oxide, **HgO**, is formed as a red powder by the combination of mercury with oxygen at a temperature of about 300°. It is commonly prepared by heating mercuric nitrate gently.

$$2 \, Hg(NO_3)_2 \longrightarrow 2 \, HgO + 4 \, NO_2 + O_2$$
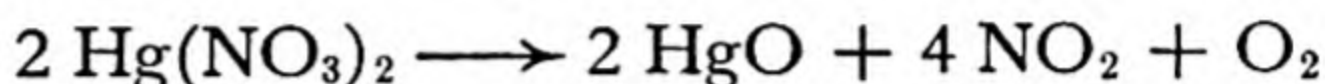
A finely divided yellow form of this oxide is precipitated by the reaction of sodium hydroxide with mercuric salts.

$$Hg^{++} + 2 \, OH^- \longrightarrow HgO \downarrow + H_2O$$
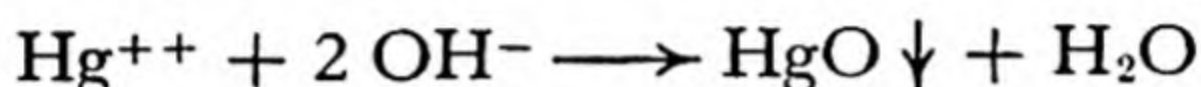
Nitrates of Mercury. *Mercurous nitrate*, **Hg₂(NO₃)₂**, the common soluble mercurous salt, is prepared by the reaction of moderately concentrated nitric acid with mercury.

$$8 \, H^+ + 2 \, NO_3^- + 6 \, Hg \longrightarrow 2 \, NO + 3 \, Hg_2^{++} + 4 \, H_2O$$
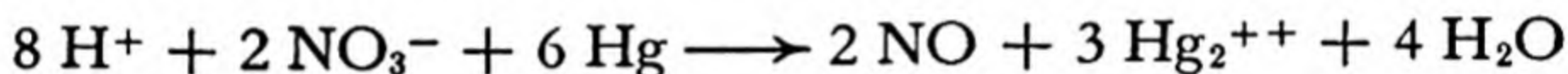
Mercurous nitrate hydrolyzes in aqueous solution with the formation of the slightly soluble hydroxynitrate.

$$Hg_2^{++} + H_2O + NO_3^- \rightleftharpoons Hg_2OHNO_3 \downarrow + H^+$$
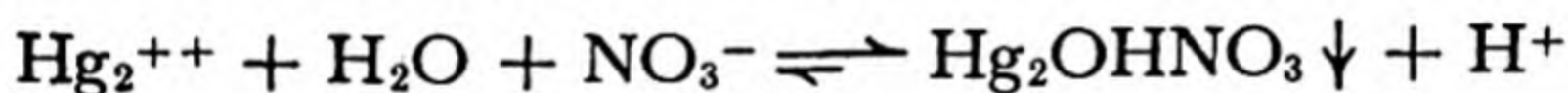
An excess of nitric acid is added to solutions of mercurous nitrate to prevent hydrolysis. Mercurous nitrate is slowly oxidized by nitric acid to form the mercuric salt. Hence, an excess of free mercury is usually placed in solutions of mercurous nitrate in order to reduce continuously the mercuric ions formed by this reaction.

Mercuric nitrate, **Hg(NO₃)₂**, is formed by the reaction of an excess of hot nitric acid with mercury or with mercurous nitrate.

$$8 \, H^+ + 2 \, NO_3^- + 3 \, Hg \longrightarrow 2 \, NO + 3 \, Hg^{++} + 4 \, H_2O$$
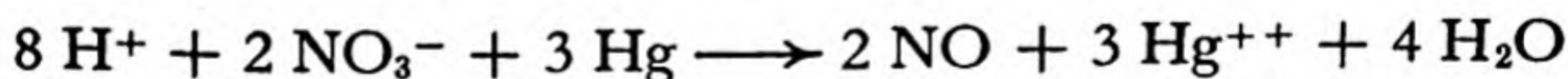
Mercuric nitrate also hydrolyzes to produce the slightly soluble hydroxynitrate or oxynitrate, unless an excess of the acid is kept in the solution.

$$Hg^{++} + H_2O + NO_3^- \rightleftharpoons HgOHNO_3 \downarrow + H^+$$
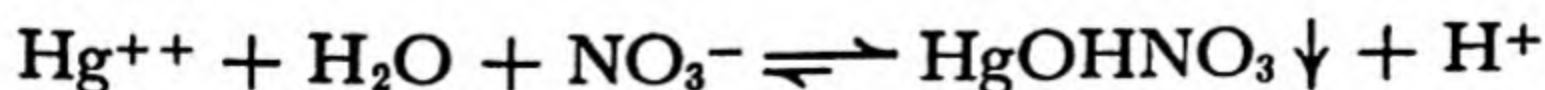
Mercuric nitrate is the common reagent supplying mercuric ions.

Chlorides of Mercury. *Mercurous chloride*, **Hg₂Cl₂**, is the most important of the mercurous salts. It is prepared commercially by

sublimation from a mixture of mercuric sulfate, mercury, and sodium chloride.

$$HgSO_4 + Hg + 2\,NaCl \longrightarrow Hg_2Cl_2 \uparrow + Na_2SO_4$$
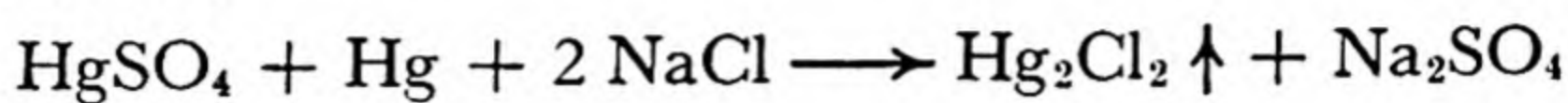
This substance, known as *calomel*, is used medicinally to stimulate the liver. The action of light causes mercurous chloride to decompose, forming a mixture of mercuric chloride and mercury.

$$Hg_2Cl_2 \longrightarrow Hg + HgCl_2$$
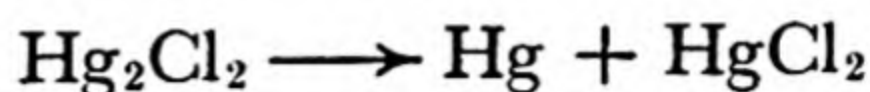
These products are poisonous. Mercurous chloride is only slightly soluble, so that it may be precipitated by the reaction of soluble mercurous compounds with chlorides.

$$Hg_2^{++} + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 \downarrow$$
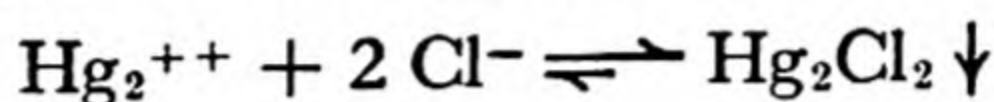
It is also produced by the mild reduction of mercuric ions with a limited proportion of stannous chloride.

$$2\,Hg^{++} + Sn^{++} + 8\,Cl^- \longrightarrow Hg_2Cl_2 + SnCl_6^{--}$$
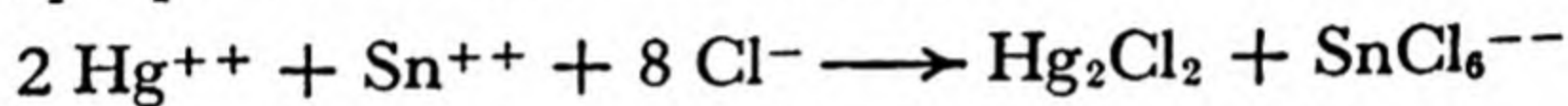
Mercuric chloride, $HgCl_2$, also called *bichloride of mercury* and *corrosive sublimate*, is prepared by sublimation from a mixture of mercuric sulfate and sodium chloride.

$$HgSO_4 + 2\,NaCl \longrightarrow HgCl_2 \uparrow + Na_2SO_4$$
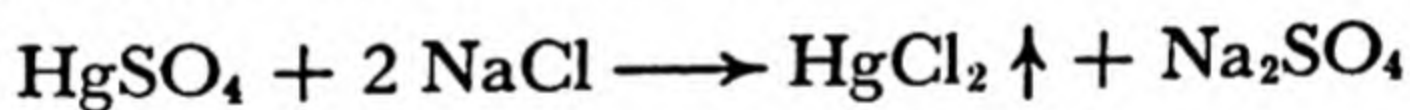
The solid is a white crystalline substance, only moderately soluble in water. It yields low concentrations of mercuric ions due, in part at least, to the formation of the mercuric chloride complex ion, $HgCl_4^{--}$. Mercuric chloride in dilute solution is used as a germicidal agent for the irrigation of wounds. Mercuric chloride is highly poisonous, and care must be exercised to avoid taking it internally. Tablets for the preparation of the germicidal solution are generally colored blue by an inactive coloring material. Mercuric chloride forms insoluble compounds with proteins, and, consequently, the white of egg is used as an antidote in cases of poisoning by this substance.

Mercuric Sulfate. $HgSO_4$. This salt is prepared by the reaction of mercury with hot concentrated sulfuric acid.

$$Hg + 2\,H_2SO_4 \longrightarrow HgSO_4 + 2\,H_2O + SO_2$$
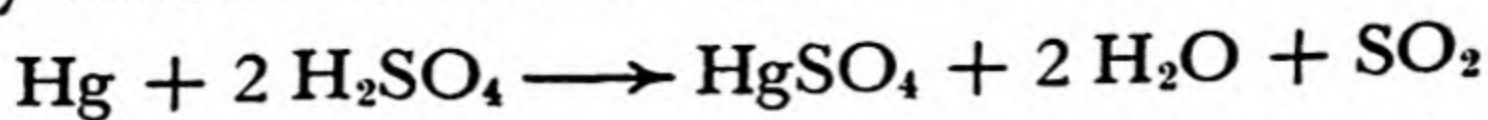
This compound is used in the production of calomel and of bichloride of mercury.

Mercuric Sulfide. HgS. The natural mineral, and the product prepared by sublimation from a mixture of mercury and sulfur, is a red crystalline solid, but the precipitated sulfide is black. It is the least soluble of the common metal sulfides and is not dissolved by hydrochloric acid or by nitric acid. It is dissolved by aqua regia, with the formation of the mercuric chloride complex ion.

$$[2\ H^+ + NO_3^- + \epsilon \longrightarrow NO_2 + H_2O] \times 2$$
$$HgS + 4\ Cl^- \longrightarrow HgCl_4^{--} + S + 2\ \epsilon$$
$$\overline{4\ H^+ + 2\ NO_3^- + HgS + 4\ Cl^- \longrightarrow 2\ NO_2 + HgCl_4^{--} + S + 2\ H_2O}$$
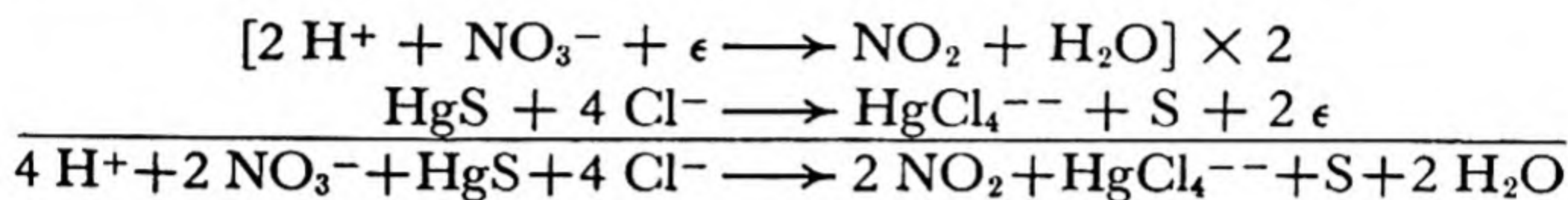
Mercuric ions yield double salts with chloride and sulfide ions, such as $HgCl_2(HgS)_2$. This substance is white but changes to an orange and finally a black precipitate as conversion to the simple sulfide proceeds.

Mercuric Fulminate. Hg(ONC)₂. This compound is formed by the reaction of ethanol with a hot solution of mercuric nitrate and nitric acid. It is insoluble in both ethanol and water. It is a violent and dangerous explosive which detonates by friction when dry. It should not be handled by the inexperienced. It is used as an initiator or primer to cause the detonation of high explosives.

EXERCISES

1. Describe the production of zinc by the retort process and by the electrolytic process. What are the respective advantages of the two processes?
2. How is cadmium commonly prepared? Explain the fact that it is prepared as a by-product of the production of other metals rather than by the smelting of cadmium ores.
3. Describe the preparation and purification of metallic mercury.
4. Compare the structures of the atoms of the elements of Group II–B with those of the elements of Group II.
5. Illustrate by equations the important reactions of zinc, cadmium, and mercury.
6. Explain the usefulness of zinc and cadmium in the protection of iron from corrosion.
7. Explain in terms of the solubility product principle and ionic equilibria in solution why zinc hydroxide dissolves in hydrochloric acid, in sodium hydroxide, in a solution of ammonia, and in a solution of potassium cyanide.
8. Compare the properties of the cadmium ion with those of the zinc ion.
9. Explain the fact that solutions of the sulfates, chlorides, and nitrates of zinc and cadmium are acidic.
10. Represent by equations suitable reactions for the preparation of (a) zinc chloride, (b) zinc sulfate, (c) zinc sulfide, (d) zinc ammonium phosphate, (e) zinc oxide.

11. Explain why the mercurous ion has the composition Hg_2^{++}.
12. Write equations to represent the reaction of mercury with (*a*) nitric acid, (*b*) sulfuric acid, and (*c*) sulfur.
13. Explain the fact that an excess of nitric acid is added to solutions of the nitrates of mercury. Why is free mercury placed in the bottles containing solutions of mercurous salts?

SUPPLEMENTARY READINGS

Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940, chap. VIII.

Hayward, C. R., *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1929, chaps. III, VII, XI.

Hanley, H. R., "Story of Zinc," *J. Chem. Education* **10,** 600, 682 (1933); **11,** 33, 111 (1934).

Chapter 32

TRANSITION ELEMENTS
OF GROUPS V–B, VI–B, AND VII–B

The electron distribution in the atoms of the transition elements has been discussed in preceding chapters, pages 197, 483, and 501. The elements of Groups III–B and IV–B of the periodic system closely resemble the elements of Groups III and IV, respectively. Groups I–B and II–B are well-defined groups of elements, but they exhibit little similarity to the elements of Groups I and II, respectively. The elements of the intervening B groups are: V–B, *vanadium, columbium,* and *tantalum;* VI–B, *chromium, molybdenum, tungsten,* and *uranium;* VII–B, *manganese, masurium,* and *rhenium;* and VIII–B, *iron, cobalt, nickel,* and *the platinum metals.* Among the transition elements, group relationships become less prominent, and similarities between elements of consecutive atomic numbers become more apparent as the number of electrons in the outer shell of the atomic kernels increases.

The Production of the Metals. The principal minerals used in the production of these metals are indicated in Table 42.

TABLE 42. ORES OF THE TRANSITION METALS OF GROUPS V–B, VI–B, VII–B

Element	Mineral	Formula
Vanadium	Vanadinite	$[Pb_3(VO_4)_2]_3PbCl_2$
Columbium	Columbite	$Fe(CbO_3)_2$
Tantalum	Tantalite	$Fe(TaO_3)_2$
Chromium	Chromite	$Fe(CrO_2)_2$
Molybdenum	Molybdenite	MoS_2
Tungsten	Wolframite	$FeWO_4MnWO_4$
Manganese	Pyrolusite	MnO_2

Metallic uranium and rhenium are not important. Usually, the metals are prepared by the reduction of their oxides with hydrogen or with aluminum. Molybdenum and chromium may also be

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produced by the reduction of the oxides with carbon. Consequently, the preparation of the oxide is necessary as the first step in the production of the metals. With the exception of columbium and tantalum, the metals are generally prepared as ferroalloys for use in the steel industry. These alloys are discussed in the following chapter. There are other uses, however, for which the pure metals are in demand.

The production of tungsten for use in the form of filaments in electric light bulbs is very important. The ore is fused with sodium carbonate to form sodium tungstate. This salt is extracted by water and tungstic acid is precipitated by reaction with hydrochloric acid. The acid is reduced by heating with carbon. The melting point of tungsten is 3370°, and the metal product of reducing the oxide is a powder. To form a wire suitable for the filament of a light bulb, the powder is packed under high pressure into a short bar, and an electric current of high amperage is passed through it, causing the fine particles to sinter into a compact mass. This material may be rolled and drawn into wire of high tensile strength. The electrical resistance of the wire is so great that it is heated to incandescence by the passage of the current. Light bulbs are filled with an inactive gas, such as argon, to decrease the rate at which the hot metal in the filament evaporates.

Properties and Reactions of the Metals. These metals are hard and tough. Most of them have high melting points: tungsten, 3370°; rhenium, 3167°; tantalum, 2850°; molybdenum, 2620°; columbium, 1950°; vanadium, 1720°; chromium, 1650°; and manganese, 1260°. The metals do not tarnish extensively in air, but combine with oxygen at high temperatures. They also combine with the halogens, with sulfur, and with carbon. They do not react readily with acids to displace hydrogen.

Importance of the Metals. The most extensive use of these metals, with the exception of rhenium, uranium, and tantalum, is in the production of alloys, notably alloy steels, which are important in industry at all times and are indispensable in meeting the requirements of industry during war. Tantalum has great resistance to corrosion, a property that leads to its use in chemical plant equipment. The carbides of vanadium, columbium, tantalum, molybdenum, and tungsten are hard substances used for the manu-

facture of cutting tools and wire-drawing dies. Tantalum absorbs gases so readily that it is used in the vacuum tube industry, particularly in the production of electronic tubes. Manganese is used in the preparation of the alloy, manganin, which contains 84 per cent of copper, 12 per cent of manganese, and 4 per cent of nickel. This alloy is used in electrical instruments because its resistance is affected but slightly by changes in temperature. Further important alloys are mentioned when their other component metals are discussed.

The greater part of several of these metals has been obtained from foreign sources, *e.g.*, chromium from Turkey, New Caledonia, Rhodesia, and other countries; tungsten from China; high grade manganese ore from Russia and India; and vanadium from Peru. The demand for some of these metals is now several times greater than before the war, while many of the former sources of supply are no longer available. Hence, these metals have assumed a position of great strategic importance, and the domestic production has been greatly increased. New deposits of some of the metals have been located, *e.g.*, chromium ores in Montana and tungsten ores in Idaho. Deposits, formerly almost inaccessible because of transportation difficulties, are being worked as, for example, vanadium ores in Colorado. Methods for producing the metals from low grade ores are employed, as in the production of manganese by a leaching process followed by electrodeposition from solution. The available supply may be greatly extended by substitution, *e.g.*, molybdenum, which is plentiful, replacing about half of the tungsten in cutting steels.

Oxidation States of the Metals. The atoms of the elements in these groups contain two electrons in the outermost energy region. They also have three to five electrons, depending on the atomic number, in the outer shell of the atomic kernel in excess of those in the inert gas structure. The oxidation numbers of the elements depend not only on the number of electrons in the valence shell but also on these additional electrons in the atomic kernel. Consequently, the elements are characterized by a number of oxidation states ranging from 2 + to the group number.

A transition in chemical nature is shown by these elements, from metallic character in low oxidation states to nonmetallic

character in high states. This relationship between the compounds of a single element is analogous to that previously noted in a group of elements. The chemistry of a particular element in the transition series is, therefore, complicated not only by the number of oxidation states and the differences between compounds in the different states but also by the oxidation-reduction reactions involved in change from one state to another. Because of the dual nature of these elements, the concentrations of hydrogen and hydroxide ions in solution play an important role in determining both the nature of the oxidation-reduction products and the activity of the reactants. The compounds of chromium and manganese serve to illustrate these relationships which are general among the transition elements, particularly those in the vanadium, chromium, and manganese groups.

COMPOUNDS OF CHROMIUM

Chromium forms compounds in three oxidation states. These states and the formulas of representative compounds in each are listed in Table 43.

TABLE 43. CHROMIUM COMPOUNDS

Oxidation State	Oxide	Hydroxide	Reaction	Ions
2 +	CrO	$Cr(OH)_2$	Basic	Cr^{++}
3 +	Cr_2O_3	$Cr(OH)_3$	Amphoteric	$\begin{cases} Cr^{+++} \\ Cr(OH)_4^- \end{cases}$
6 +	CrO_3	$\begin{cases} H_2CrO_4 \\ H_2Cr_2O_7 \end{cases}$	$\begin{cases} \text{Acidic} \\ \text{Acidic} \end{cases}$	$\begin{cases} CrO_4^{--} \\ Cr_2O_7^{--} \end{cases}$

The compounds in the 3 + and 6 + states are the most stable and important compounds of the element.

Chromous Compounds. Chromous salts may be prepared by the reduction of chromic salts by zinc in acidic solution. The chloride and sulfate are soluble salts which may be used as sources of the chromous ion. Solutions containing this ion are blue in color. The hydroxide is slightly soluble and is basic in properties. Chromous compounds are similar to ferrous compounds, except that the chromous ion is less stable than the ferrous ion and is oxidized by mild oxidizing agents.

Chromic Compounds and Chromites. The chromic ion has a coordination number of 6. It commonly exists in acidic solution as the complex hexahydrate, $Cr(H_2O)_6^{+++}$. Solutions containing this ion have a violet color. The complex ion contains anions of the salt in hot and concentrated solutions, *e.g.*, $Cr(H_2O)_4Cl_2^+$. Such solutions are green in color. Silver nitrate causes the precipitation of only one third of the chlorine in the green solution of chromic chloride. The common chromic salts are the chloride, $CrCl_3(H_2O)_6$, the sulfate, $Cr_2(SO_4)_3(H_2O)_{18}$, and chrome alum, $KCr(SO_4)_2(H_2O)_{12}$. Chromic salts are usually produced by reduction of dichromates in acidic solution. They may also be formed by reactions of the hydroxide with appropriate acids.

Chromic ions hydrolyze to form acidic solutions.

$$Cr(H_2O)_6^{+++} + H_2O \rightleftharpoons Cr(H_2O)_5(OH)^{++} + H_3O^+$$
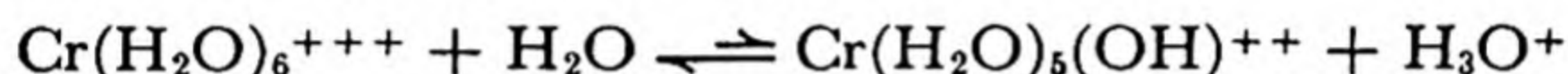
The addition of a weak base or a limited proportion of a strong base causes the precipitation of the *hydrous oxide*. This product is commonly called *chromic hydroxide* and is represented by the formula $Cr(OH)_3$ or $Cr(H_2O)_3(OH)_3$, although the actual proportions of water may vary.

$$Cr(H_2O)_6^{+++} + 3\ C_2H_3O_2^- \rightleftharpoons Cr(H_2O)_3(OH)_3 \downarrow + 3\ HC_2H_3O_2$$
$$Cr(H_2O)_6^{+++} + 3\ OH^- \rightleftharpoons Cr(H_2O)_3(OH)_3 \downarrow + 3\ H_2O$$
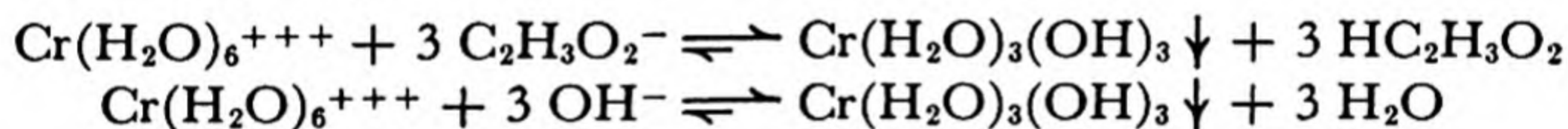
The hydroxide is amphoteric, reacting with strong acids to form chromic ions and with strong bases to form metachromites.

$$Cr(H_2O)_3(OH)_3 \downarrow + 3\ H_3O^+ \longrightarrow Cr(H_2O)_6^{+++} + 3\ H_2O$$
$$Cr(H_2O)_3(OH)_3 \downarrow + OH^- \longrightarrow Cr(H_2O)_2(OH)_4^- + H_2O$$
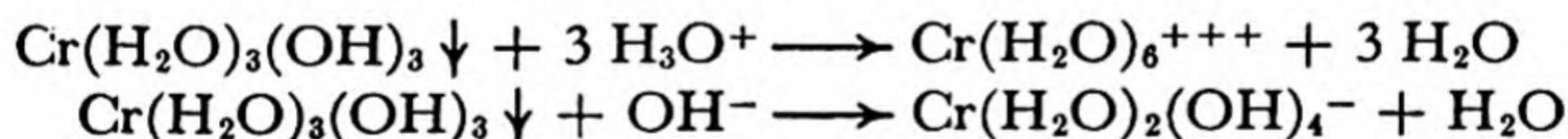
The metachromite solutions are green in color. This ion is decomposed by reaction with weakly acidic solutions, forming a precipitate of the hydroxide.

$$Cr(H_2O)_2(OH)_4^- + NH_4^+ \rightleftharpoons Cr(H_2O)_3(OH)_3 \downarrow + NH_3$$
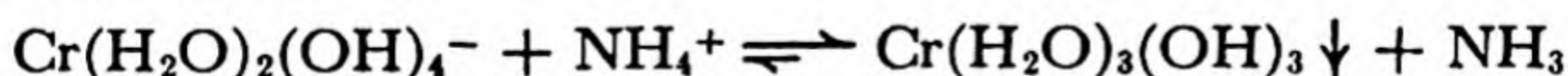
The hydroxide may also be precipitated by the hydrolysis of the metachromite, unless the solution is too strongly basic.

$$Cr(H_2O)_2(OH)_4^- + H_2O \rightleftharpoons Cr(H_2O)_3(OH)_3 \downarrow + OH^-$$
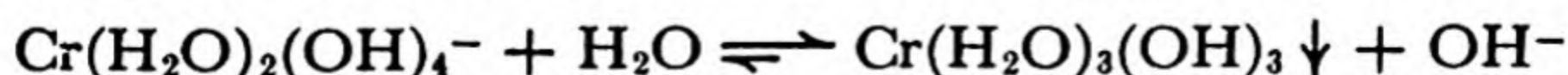
Chromic oxide, Cr_2O_3, is the most stable of the oxides of chromium toward heat. It is the product formed by heating the metal or its

other oxides in air. It is a finely divided green powder which is important as a paint pigment.

Chromates and Dichromates. In its high state of oxidation, chromium exhibits the properties of a nonmetallic element. *Chromic anhydride*, CrO_3, reacts with water to form chromic acid, H_2CrO_4, and dichromic acid, $H_2Cr_2O_7$. Chromic anhydride is a red crystalline oxide formed by the reaction of concentrated sulfuric acid with potassium dichromate.

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2O + 2\ CrO_3$$
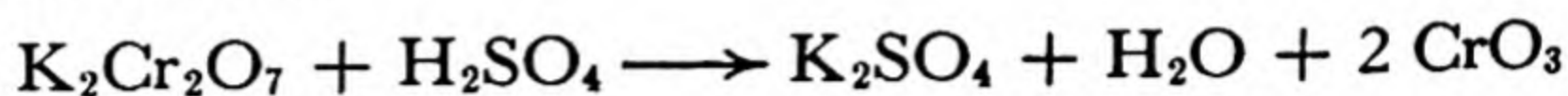
Potassium chromate, K_2CrO_4, may be prepared by heating the mineral *chromite*, $Fe(CrO_2)_2$, with potassium carbonate in a current of air.

$$4\ Fe(CrO_2)_2 + 8\ K_2CO_3 + 7\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ K_2CrO_4 + 8\ CO_2$$
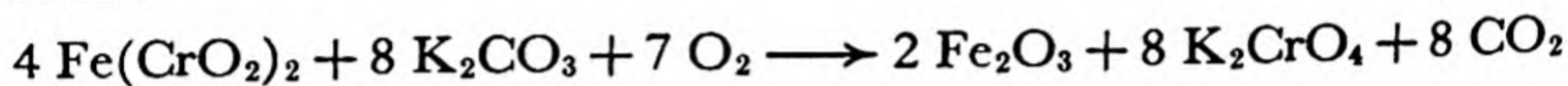
Potassium chromate is leached from this product and purified by recrystallization. Solutions of the chromates are yellow due to chromate ions. Barium chromate and lead chromate are precipitated by the reaction of a solution of a chromate with barium and lead ions, respectively.

$$Ba^{++} + CrO_4^{--} \rightleftharpoons BaCrO_4 \downarrow$$
$$Pb^{++} + CrO_4^{--} \rightleftharpoons PbCrO_4 \downarrow$$
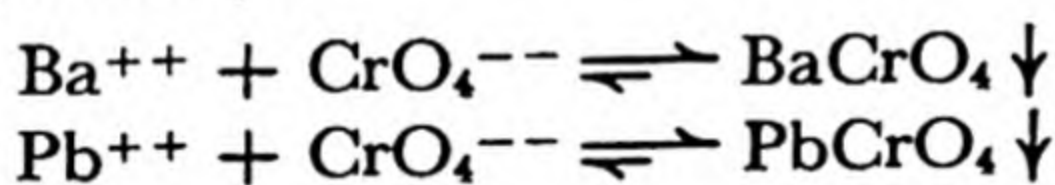
Chrome yellow, $PbCrO_4$, chrome red, Pb_2OCrO_4, and zinc chromate, $ZnCrO_4$, are important paint pigments.

Soluble chromates are hydrolyzed with the formation of an equilibrium mixture of the chromate and dichromate.

$$2\ CrO_4^{--} + 2\ H_2O \rightleftharpoons Cr_2O_7^{--} + 2\ OH^-$$
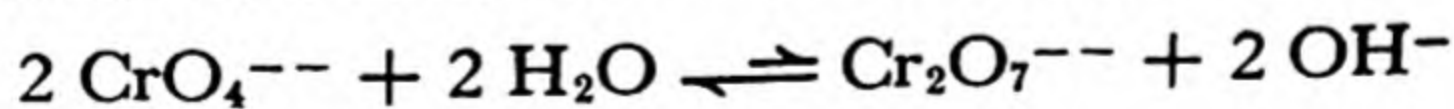
The addition of an acid increases the concentration of the dichromate ion, producing an orange colored solution. The dichromate may be crystallized from the acidic solution.

$$2\ CrO_4^{--} + 2\ H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$
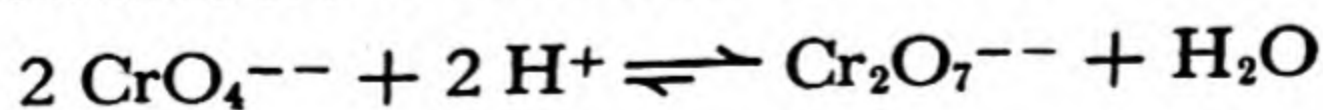
An excess of a strong base causes the conversion of the dichromate into the chromate.

$$Cr_2O_7^{--} + 2\ OH^- \rightleftharpoons 2\ CrO_4^{--} + H_2O$$
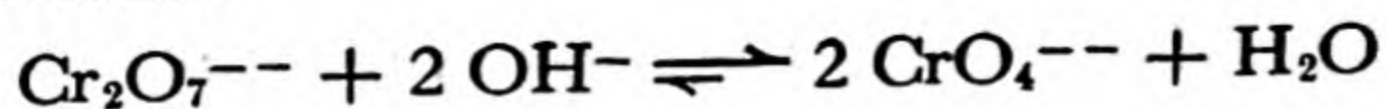
Sodium dichromate is employed in the tanning of leather. The hide is soaked in a solution of the dichromate, and chromic hydroxide is

deposited in the pores when this compound is reduced. Dichromates are active oxidizing agents, which have many uses in analytical chemistry. A concentrated solution of dichromic acid, prepared by the reaction of a solid dichromate with concentrated sulfuric acid, is used as a cleaning solution for laboratory glassware.

Oxidation-Reduction Involving Chromium Compounds. The oxidation of chromium compounds from the 3 + to the 6 + state is a reversible change that may be carried out in either basic or acidic solution.

$$Cr(OH)_4^- + 4\,OH^- \longrightarrow CrO_4^{--} + 4\,H_2O + 3\,\epsilon$$
$$2\,Cr^{+++} + 7\,H_2O \longrightarrow Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon$$
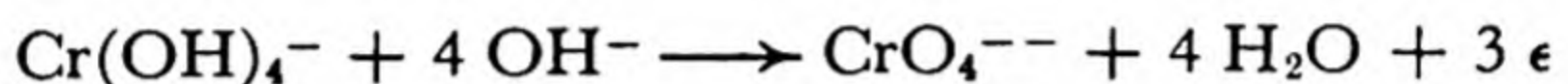
Dichromate ions in acidic solution have much higher oxidizing activity than chromate ions in neutral or basic solution. Conversely, metachromite ions in basic solution have greater reducing activity than chromic ions in acidic solution. Therefore, the oxidation of chromic compounds is usually carried out in basic solution. Sodium hypochlorite, sodium peroxide, and hydrogen peroxide are suitable oxidizing agents for use in basic solution.

$$[ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-] \times 3$$
$$\underline{[Cr(OH)_4^- + 4\,OH^- \longrightarrow CrO_4^{--} + 4\,H_2O + 3\,\epsilon] \times 2}$$
$$3\,ClO^- + 2\,Cr(OH)_4^- + 2\,OH^- \longrightarrow 3\,Cl^- + 2\,CrO_4^{--} + 5\,H_2O$$
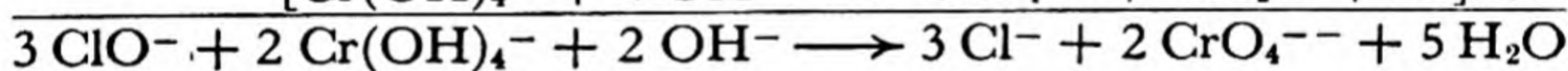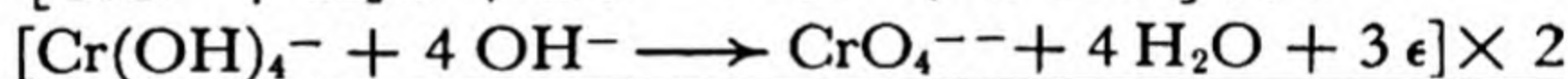
Anhydrous chromic oxide does not dissolve readily in basic solutions. Consequently, the production of the chromate from the oxide is best accomplished by oxidation in the presence of a fused alkali hydroxide or carbonate. Under these conditions suitable oxidizing agents are the alkali metal nitrates and chlorates. The equations for oxidation-reduction may be derived in terms of the changes in oxidation numbers. (See page 417.)

$$\overset{Cl^{5+}}{Cr_2O_3} + KClO_3 + 4\,KOH \overset{(-6)}{\underset{(+6)}{\longrightarrow}} 2\,K_2CrO_4 + \overset{Cl^-}{KCl} + 2\,H_2O$$
$$\underset{2\,Cr^{3+}}{} \qquad\qquad\qquad\qquad\qquad \underset{2\,Cr^{6+}}{}$$
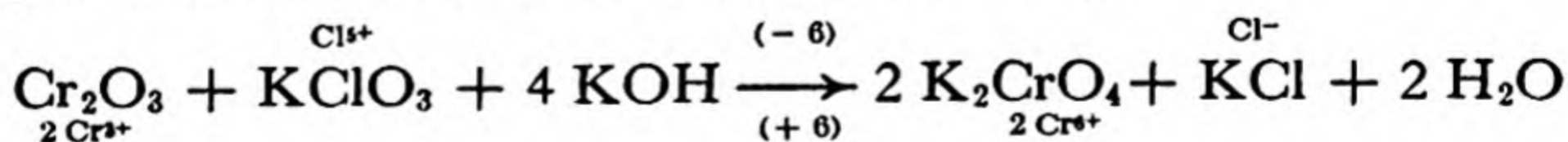
The dichromates are active oxidizing agents in acidic solution, reacting with different classes of reducing agents to form chromic ions.

$$Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon \longrightarrow 2\,Cr^{+++} + 7\,H_2O$$
$$\underline{[2\,I^- \longrightarrow I_2 + 2\,\epsilon] \times 3}$$
$$Cr_2O_7^{--} + 14\,H^+ + 6\,I^- \longrightarrow 2\,Cr^{+++} + 3\,I_2 + 7\,H_2O$$
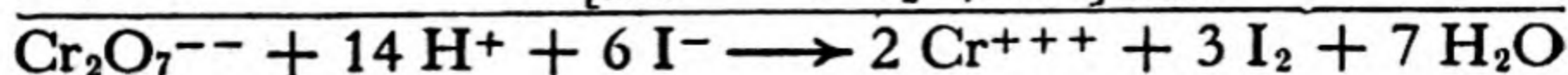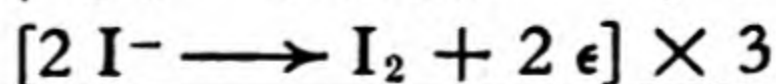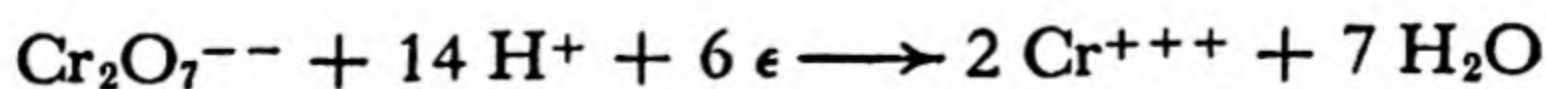
Chromates may be reduced by strong reducing agents in basic solution with the formation of metachromites.

$$[CrO_4^{--} + 4\,H_2O + 3\,\epsilon \longrightarrow Cr(OH)_4^- + 4\,OH^-] \times 2$$
$$\underline{[SO_3^{--} + 2\,OH^- \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon] \times 3}$$
$$2\,CrO_4^{--} + 3\,SO_3^{--} + 5\,H_2O \longrightarrow 2\,Cr(OH)_4^- + 3\,SO_4^{--} + 2\,OH^-$$
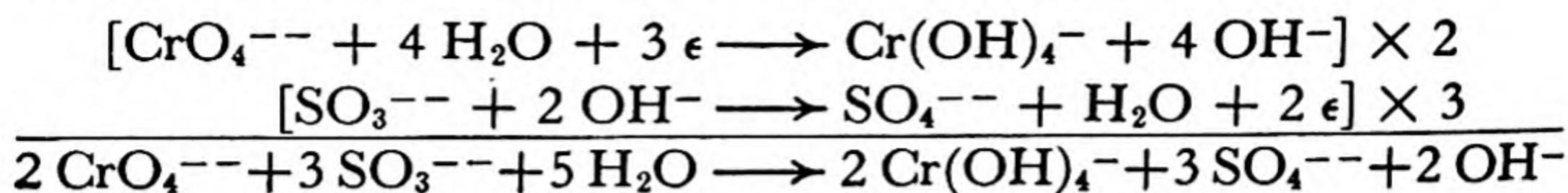
COMPOUNDS OF MANGANESE

Manganese may form compounds in five oxidation states. These states and the formulas of typical compounds are shown in Table 44.

TABLE 44. MANGANESE COMPOUNDS

Oxidation State	Oxide	Hydroxide	Reaction	Ions
2	MnO	$Mn(OH)_2$	Basic	Mn^{++}
3	Mn_2O_3	$Mn(OH)_3$	Basic	Mn^{+++}
4	MnO_2	$Mn(OH)_4$	Amphoteric	MnO_3^{--}
6	MnO_3	H_2MnO_4	Acidic	MnO_4^{--}
7	Mn_2O_7	$HMnO_4$	Acidic	MnO_4^-

Compounds containing the manganic ion, Mn^{+++}, are unstable and produce the manganous ion and manganese dioxide.

$$2\,Mn^{+++} + 2\,H_2O \longrightarrow Mn^{++} + MnO_2 + 4\,H^+$$
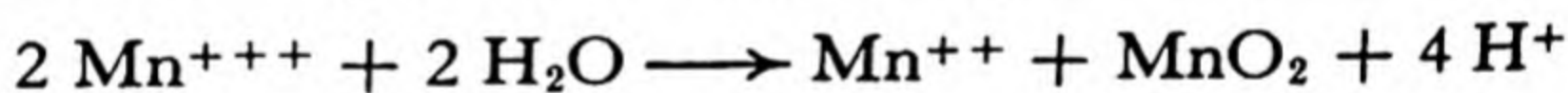
This oxidation state of manganese is unimportant and will be omitted from further discussion.

Manganous Compounds. Manganese exhibits the behavior of a metallic element in the divalent state and yields compounds similar to those of magnesium and ferrous iron. The common manganous salts are the chloride and the sulfate. These may be formed by the reduction of manganese dioxide in acidic solution. Insoluble manganous compounds, such as the carbonate, the sulfide, the phosphate, and the hydroxide, are prepared by precipitation. The manganous ion yields a white crystalline precipitate of manganous ammonium phosphate in the presence of a soluble phosphate and ammonia.

$$Mn^{++} + HPO_4^{--} + NH_3 \rightleftharpoons MnNH_4PO_4 \downarrow$$
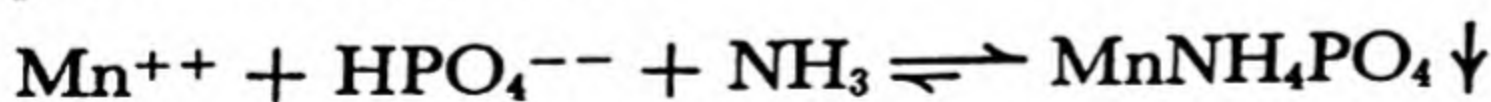
The presence of ammonium ions in an ammoniacal solution reduces the concentration of the hydroxide ions so greatly that manganous hydroxide does not precipitate. The addition of sodium

hydroxide to a solution of a manganous salt causes the precipitation of manganous hydroxide.

$$Mn^{++} + 2\,OH^- \rightleftharpoons Mn(OH)_2\downarrow$$
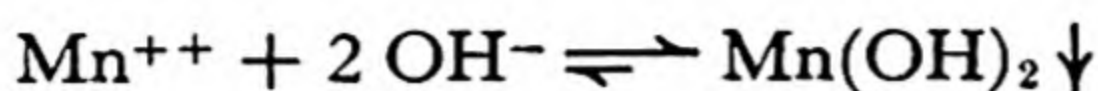
Manganous hydroxide is a white gelatinous precipitate that rapidly darkens in contact with air, due to the formation of the brown manganous manganite, $MnMnO_3$, or black manganese dioxide, MnO_2. Oxidation, forming manganese dioxide, is completed by reaction with sodium hypobromite or hypochlorite.

$$Mn(OH)_2 + BrO^- \longrightarrow MnO_2\downarrow + Br^- + H_2O$$
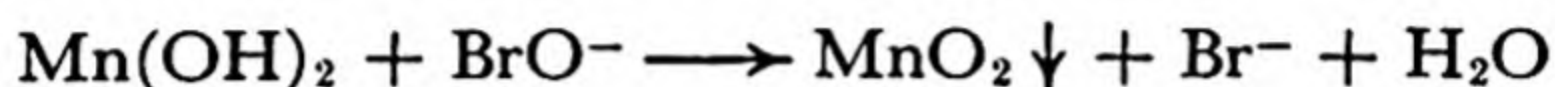
Manganous oxide may be oxidized to form the manganate by fusion with potassium nitrate and a basic substance.

$$\overset{N^{5+}}{2\,KNO_3} + \underset{Mn^{2+}}{MnO} + K_2CO_3 \overset{2\times(-2)}{\underset{+4}{\longrightarrow}} \overset{N^{3+}}{2\,KNO_2} + \underset{Mn^{6+}}{K_2MnO_4} + CO_2$$
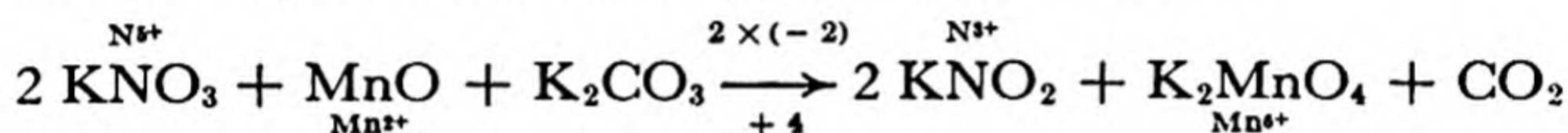
Manganous salts may be oxidized by strong oxidizing agents, such as sodium bismuthate, in acidic solution, with the formation of the permanganate.

$$[BiO_3^- + 6\,H^+ + 2\,\epsilon \longrightarrow Bi^{+++} + 3\,H_2O] \times 5$$
$$\underline{[Mn^{++} + 4\,H_2O \longrightarrow MnO_4^- + 8\,H^+ + 5\,\epsilon] \times 2}$$
$$5\,BiO_3^- + 14\,H^+ + 2\,Mn^{++} \longrightarrow 5\,Bi^{+++} + 2\,MnO_4^- + 7\,H_2O$$
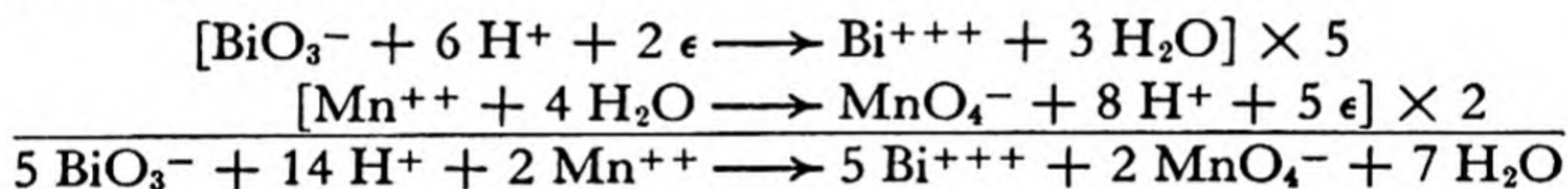
Manganese Dioxide. Manganites. The most important compound of manganese in the 4 + state of oxidation is the dioxide, which occurs as the natural mineral *pyrolusite*. Although this oxide is both basic and acidic, it is not active in either respect. It reacts with cold concentrated hydrochloric acid to form a green solution of the tetrachloride.

$$MnO_2 + 4\,H^+ + 4\,Cl^- \longrightarrow MnCl_4 + 2\,H_2O$$
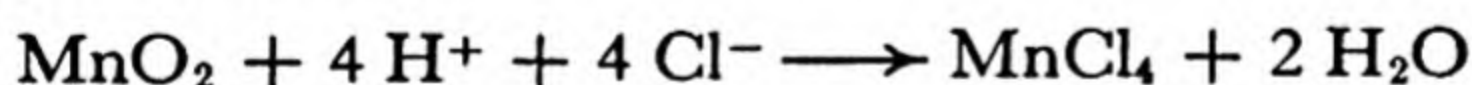
Manganese dioxide also reacts with fused bases to form manganites, *e.g.*, $CaMnO_3$.

$$CaO + MnO_2 \longrightarrow CaMnO_3$$
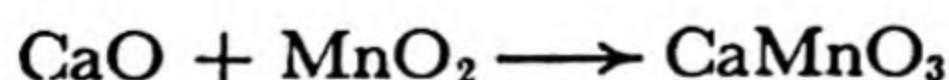
Manganese dioxide may react as both an oxidizing agent and as a reducing agent. It is reduced to form a manganous salt by reaction with warm solutions of hydrochloric acid.

$$MnO_2 + 4\,H^+ + 2\,Cl^- \longrightarrow Mn^{++} + Cl_2 + 2\,H_2O$$
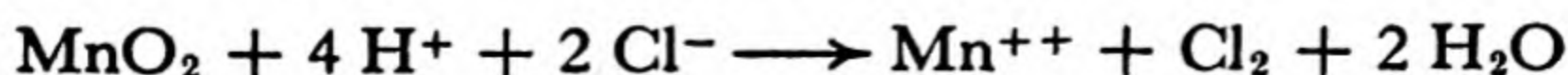
It may be oxidized to the manganate by oxidizing agents in basic fusion and to the permanganate by strong oxidizing agents in acidic solution.

Manganese dioxide is used as a drier in paint and varnish, catalyzing the oxidation of the oil. It is also employed in the glass industry to oxidize ferrous compounds. The colors of manganous and ferric silicates are complementary, so that a colorless glass may be produced from ingredients containing iron compounds by adding the proper quantity of manganese dioxide to the charge. The most widespread direct use of manganese dioxide is in the manufacture of dry cells. (See page 242.)

Manganates. The oxidation number of manganese in the manganates is 6 +, and the element is actively nonmetallic in character in this oxidation state. The salts are green, a color attributed to the manganate ion. The manganates are formed as intermediate products in the preparation of the permanganates. Potassium manganate is formed by fusing manganese dioxide with potassium hydroxide in the presence of a free supply of air.

$$2\,MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4 + 2\,H_2O$$
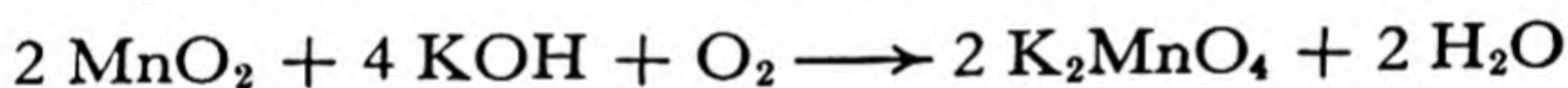
The manganates are stable in basic solution, but the addition of an acid causes the spontaneous decomposition of the manganate ion, yielding manganese dioxide and an equivalent amount of the permanganate, thus showing that the element yields more stable compounds both in its lower and higher valence states than in the manganate.

$$MnO_4^{--} + 4\,H^+ + 2\,\epsilon \longrightarrow MnO_2 + 2\,H_2O$$
$$\underline{[MnO_4^{--} \longrightarrow MnO_4^- + \epsilon] \times 2}$$
$$3\,MnO_4^{--} + 4\,H^+ \longrightarrow MnO_2 + 2\,MnO_4^- + 2\,H_2O$$
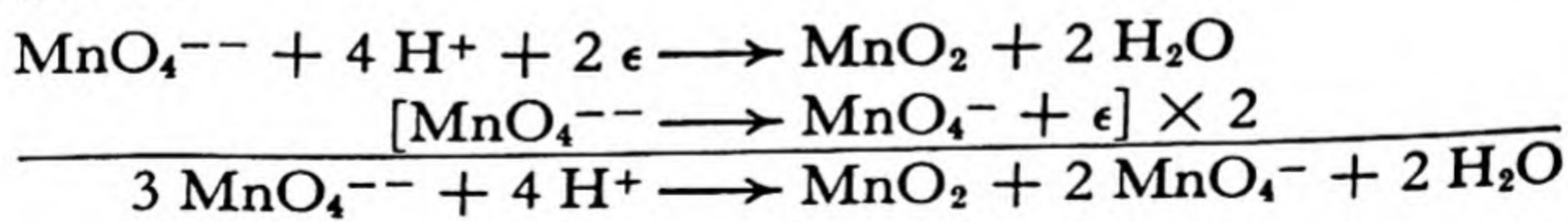
Manganates may be oxidized to permanganates at the anode during the passage of a direct current of electricity through a solution of the manganate. Solutions of the permanganates are active oxidizing agents with a number of important uses. They are also used as germicidal solutions. The reaction of cold concentrated sulfuric acid with solid potassium permanganate yields the oxide Mn_2O_7.

$$2\,KMnO_4 + 2\,H_2SO_4 \longrightarrow 2\,KHSO_4 + Mn_2O_7 + H_2O$$
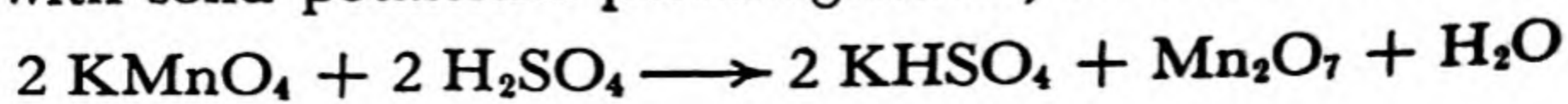
This substance is an unstable brown liquid.

Permanganates. The permanganates and permanganic acid are fairly stable in dilute solution in the absence of reducing substances. These solutions are characterized by a purple color due to the permanganate ion. In the commercial preparation of the permanganate, the manganate is first formed and is then oxidized to the permanganate by the action of chlorine in basic solution.

$$2\,MnO_4^{--} + ClO^- + H_2O \longrightarrow 2\,MnO_4^- + Cl^- + 2\,OH^-$$
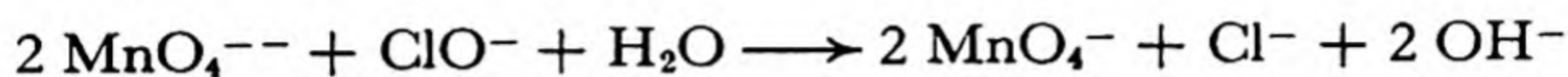
The reduction of permanganates may yield the manganate, manganese dioxide, or a manganous salt, depending on the basicity or acidity of the solution and the strength of the reducing agent. The half reactions for these changes in state of oxidation are:

$$MnO_4^- + 1\,\epsilon \longrightarrow MnO_4^{--}$$
$$MnO_4^- + 2\,H_2O + 3\,\epsilon \longrightarrow MnO_2 + 4\,OH^-$$
$$MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O$$
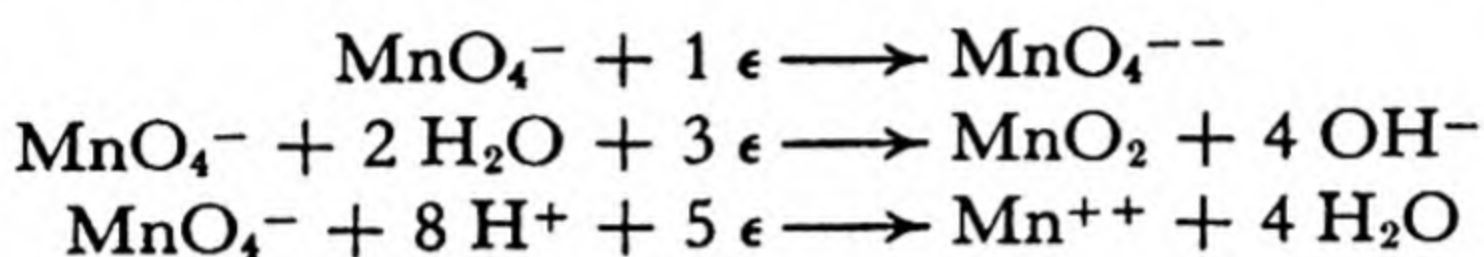
The manganate may be formed by reduction of the permanganate in basic solution, but manganese dioxide is the usual product under these conditions. The oxidizing activity of permanganates is greater in acidic than in basic solution.

Permanganates react with different classes of reducing agents *in acidic solution* to form the typical oxidation products listed in Chapter 19, page 302. The reaction of a permanganate with a ferrous salt in acidic solution produces manganic and ferric ions.

$$MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O$$
$$[Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon] \times 5$$
$$\overline{MnO_4^- + 8\,H^+ + 5\,Fe^{++} \longrightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O}$$
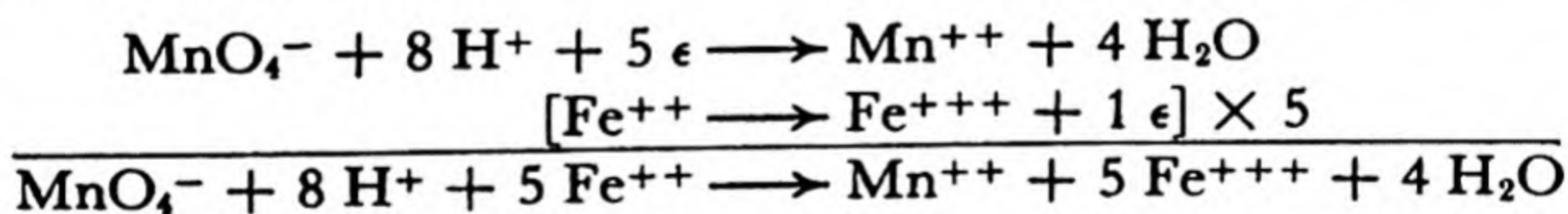
Oxalates are oxidized under the same conditions to form carbon dioxide.

$$[MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O] \times 2$$
$$[C_2O_4^{--} \longrightarrow 2\,CO_2 + 2\,\epsilon] \times 5$$
$$\overline{2\,MnO_4^- + 16\,H^+ + 5\,C_2O_4^{--} \longrightarrow 2\,Mn^{++} + 10\,CO_2 + 8\,H_2O}$$
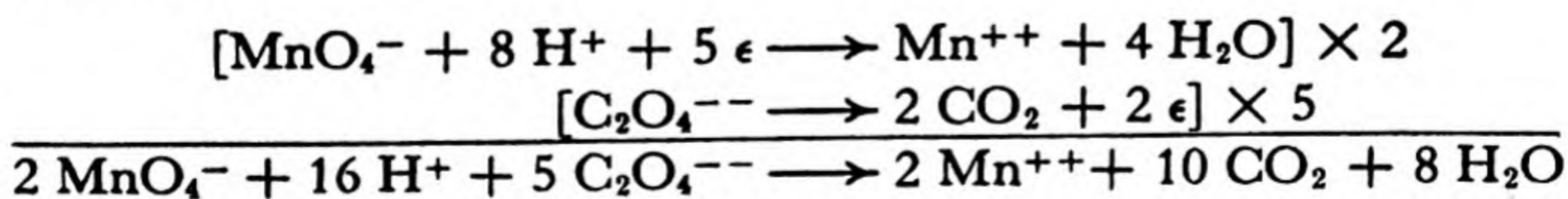
Permanganates may be used *in basic solution* for the oxidation of substances that are stronger reducing agents in basic than acidic medium. Basic permanganate may be used for the oxidation of sulfites.

$$[MnO_4^- + 2\,H_2O + 3\,\epsilon \longrightarrow MnO_2 + 4\,OH^-] \times 2$$
$$\underline{[SO_3^{--} + 2\,OH^{--} \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon] \times 3}$$
$$2\,MnO_4^- + 3\,SO_3^{--} + H_2O \longrightarrow 2\,MnO_2 + 3\,SO_4^{--} + 2\,OH^-$$
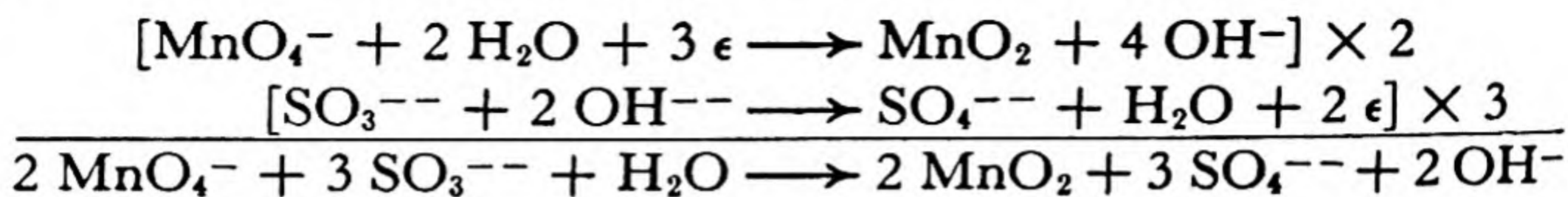
Manganous compounds may be oxidized by potassium permanganate in neutral or weakly basic solutions, with the formation of manganese dioxide.

$$[MnO_4^- + 2\,H_2O + 3\,\epsilon \longrightarrow MnO_2 + 4\,OH^-] \times 2$$
$$\underline{[Mn^{++} + 4\,OH^- \longrightarrow MnO_2 + 2\,H_2O + 2\,\epsilon] \times 3}$$
$$2\,MnO_4^- + 3\,Mn^{++} + 4\,OH^- \longrightarrow 5\,MnO_2 + 2\,H_2O$$
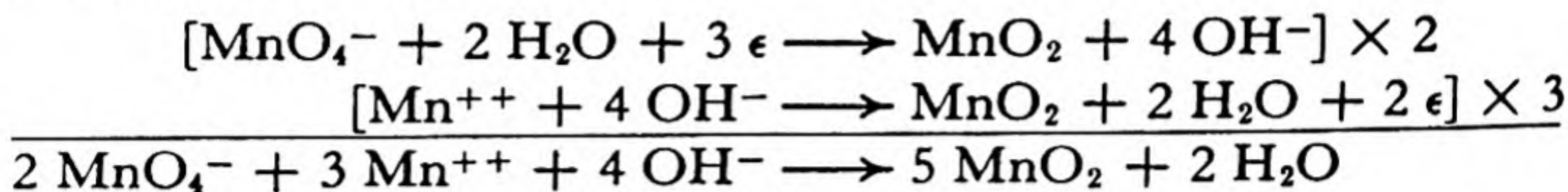
EXERCISES

1. What is meant by the transition elements? How are the elements with successive atomic numbers in the transition series related to each other in the structures of their atoms?
2. Discuss the importance of the metals in Groups V–B, VI–B, and VII–B.
3. What transition in properties is noted between the elements in their low and high oxidation states?
4. Discuss and illustrate by equations the chemical behavior of chromium and of manganese in the important states of oxidation.
5. State the conditions favorable for each of the changes indicated below, and explain why these conditions are favorable: (a) chromic compounds to chromates; (b) manganous compounds to manganese dioxide; (c) manganous compounds to manganates; (d) manganates to permanganates; (e) dichromates to chromic salts; (f) permanganates to manganese dioxide; (g) manganese dioxide to manganous compounds; (h) permanganates to manganous compounds.
6. Select oxidizing and reducing agents which may be used to bring about the changes indicated in Question 5, and represent the reactions by equations balanced by the electronic method.
7. Classify the common reducing agents according to their chemical nature. State the conditions which you consider most favorable for the oxidation of the members of each class, and explain why you think so. What product is formed in each class of reducing agents under the conditions you have selected?
8. Choose a specific reducing agent from each of the groups into which you have classified these substances. Select a different agent for the oxidation of each reducing agent under the conditions which are most favorable. Write equations, balanced by the electronic method, for the reactions involved.

SUPPLEMENTARY READINGS

Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940, chaps. XVI–XVIII.

Hayward, C. R., *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1929, chaps. XVII–XX.

Sneed, M. C., and J. L. Maynard, *General Inorganic Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, chaps. 41–44.

IRON. COBALT. NICKEL

These three metals are members of Group VIII–B of the periodic system of the elements. Unlike the elements of previously studied families, these elements have consecutive atomic numbers. The uncombined atoms have the same number of valence electrons, but differ in the number of electrons in the outer shell of the atomic kernels.

Properties and Reactions of Iron, Cobalt, and Nickel. These metals have silvery luster and are malleable and ductile. Each of these metals forms a number of important alloys. A few properties are listed in Table 45.

TABLE 45. PROPERTIES OF IRON, COBALT, AND NICKEL

Property	Iron	Cobalt	Nickel
Atomic weight	55.85	58.94	58.69
Atomic number	26	27	28
Electron structure	2, 8, 14, 2	2, 8, 15, 2	2, 8, 16, 2
Oxidation numbers	2 +, 3 +	2 +, 3 +	2 +
Melting point (° C.)	1535	1480	1452
Density at 20°, g. per ml.	7.86	8.90	8.90

The pure metals do not rust in dry air at ordinary temperatures, but they combine with oxygen, the halogens, sulfur, and carbon at elevated temperatures. Iron readily displaces hydrogen from acidic solutions, forming ferrous compounds, while cobalt and nickel react only slowly to displace hydrogen. Iron is oxidized to the ferric state by nitric acid, but cobalt and nickel form compounds in the 2 + state of oxidation by reaction with nitric acid. These metals become passive in contact with concentrated nitric acid and with acidic solutions of dichromates. In the passive condition they do not displace hydrogen from acidic solutions nor ions of less active metals from salt solutions. The passivity of the

metal is destroyed by striking it a sharp blow or by scratching the surface, and the metals then react normally.

IRON

Iron is the most important of the metals, judged by the great variety of its uses and the large quantities produced industrially each year. It is not found in the uncombined state in natural deposits near the surface of the earth, except in the form of meteoric iron which is composed of approximately 90 per cent of this metal. Iron is fourth in abundance among the elements in the outer crust of the earth. The most important iron ore is *hematite*, Fe_2O_3. Other important ores are *limonite*, $Fe_2O_3(H_2O)_3$, *magnetite*, Fe_3O_4, and *siderite*, $FeCO_3$. The most important of the iron ore deposits in the United States are the hematite ores in the Lake Superior district in Minnesota and Michigan. This district produces about 80 per cent of the iron ore. The Birmingham district in Alabama produces about 10 per cent of the hematite ore. Most of the Minnesota iron mines are open pits, but most of the mines in Michigan and Alabama are underground. Deposits are found in Colorado, California, and in other states. Magnetite ore is mined in New York and in Pennsylvania. There are important iron ore deposits in most of the industrial countries, except Japan.

The Iron of Commerce. The metal may be prepared in a high degree of purity by the reduction of its oxide with hydrogen and by the electrolysis of ferrous sulfate solutions. Pure iron has only limited industrial importance, because it is too soft and malleable to hold its shape under great strain. The pure metal cannot be tempered. The industrial importance of iron depends largely on the fact that the presence of small proportions of specified ingredients, notably carbon, modifies the properties of the metal to a great extent. The most familiar varieties of commercial iron are cast iron, steel, and wrought iron. These commercial materials do not have specific composition, but are products of specific furnace operations. The composition of steel, for example, may be varied over wide limits to develop the properties required for particular uses.

The production of the finer grades of iron from the ore requires

more than one furnace process. In the first process, the metal is secured from its oxide ore by reduction, using an excess of carbon. The ore contains reducible substances in addition to the iron oxide, and some of the reduction products contaminate the iron. At the

```
                          ┌─────────────┐
                          │ Hematite Ore│
                          └─────────────┘
                                │
                          Blast Furnace
                         (Coke and Flux)
          ┌─────────────────────┼─────────────────────┐
          ▼                      ▼                      ▼
        Slag               ┌──────────┐               Gas
      (Discard)            │ Pig Iron │              (Fuel)
                           └──────────┘
        ┌────────────────────┼────────────────────┐
        ▼                    │                     ▼
  Puddling Furnace           │              Cupola Furnace
 (Pig Iron, Oxide Ore)       │             (Pig Iron, Coke,
                             │                Limestone)
   ┌──────────┐              │            ┌──────────────┐
   ▼          ▼              │            ▼              ▼
  Slag  ┌────────────┐       │      ┌──────────┐       Slag
        │Wrought Iron│       │      │ Cast Iron│
        └────────────┘       │      └──────────┘
               ┌─────────────┴─────────────┐
               ▼                           ▼
           Bessemer                 Open Hearth Furnace
           Converter               (Pig Iron, Oxide Ore,
                                   Limestone, Scrap Iron)
         ┌──────────┐              ┌──────────────┐
         ▼          ▼              ▼              ▼
        Slag    ┌───────┐       ┌───────┐       Slag
                │ Steel │       │ Steel │
                └───────┘       └───────┘
                                    │
                              Electric Furnace
                              (Basic Lining)
                               Ferroalloys
                              ┌─────────────┐
                              │ Alloy Steel │
                              └─────────────┘
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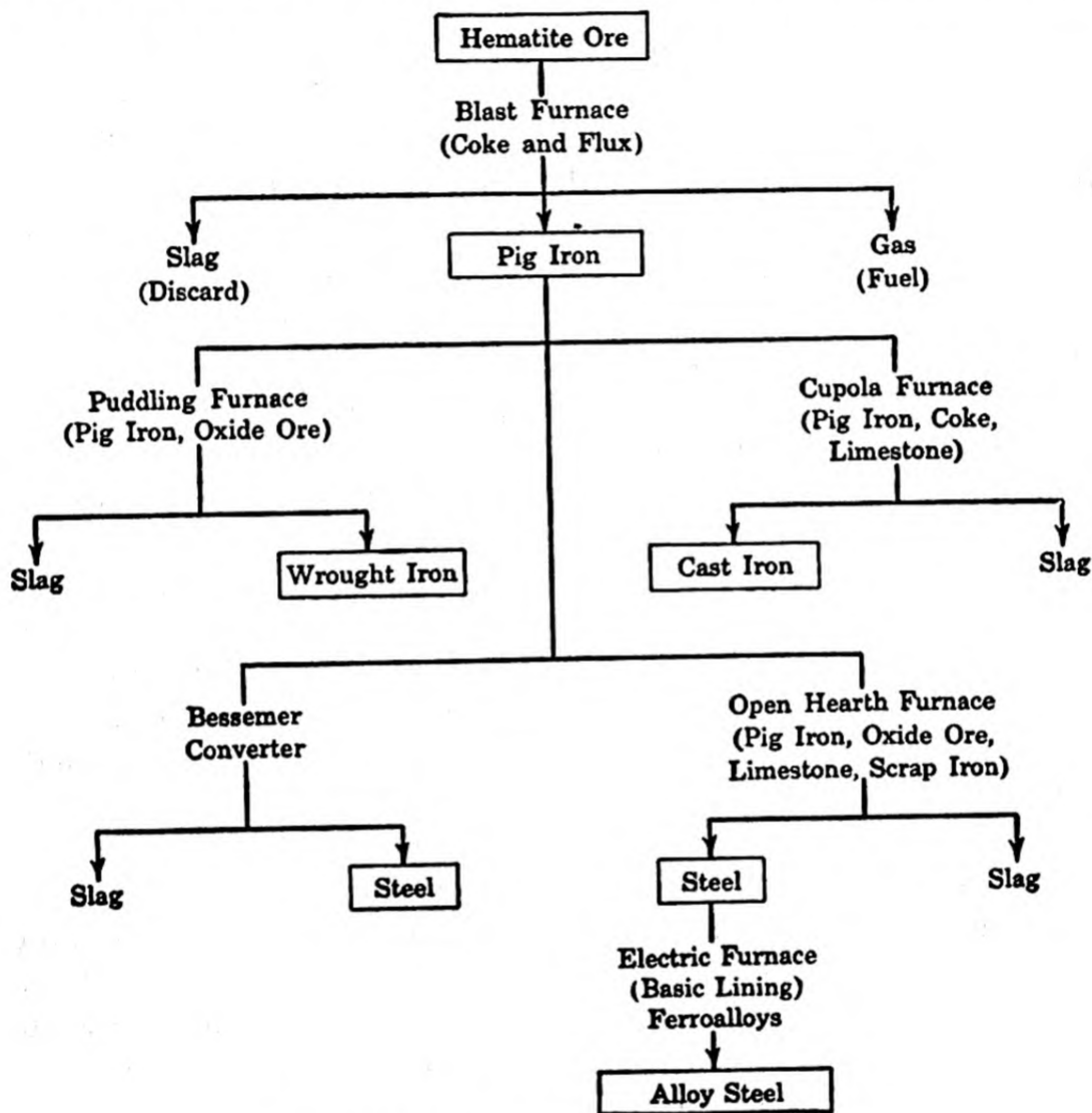
Fig. 129. Outline — Metallurgy of Iron

temperature of the furnace, carbon dissolves in molten iron and reacts with it. Hence, operations subsequent to the reduction of the ore are required to eliminate to the necessary degree the impurities that give objectionable properties, and to regulate the proportions of the beneficial impurities. The procedures are outlined in Fig. 129.

Reduction of the Ore. Iron oxide ores are smelted with coke and a flux in a blast furnace. Blast furnaces in the iron industry are approximately 100 ft. high and 25 ft. in diameter. They are constructed of steel plates and lined with firebrick. The furnaces taper, as shown in the vertical section in Fig. 130, to minimize the frictional wear of the solids on the furnace walls as the charge settles, and to provide for expansion of heated materials. The section of the furnace where the walls taper sharply is known as the "bosh." In this region, the volume of the solid contents of the furnace is greatly decreased by the burning of coke and the formation of liquid slag and iron. At the base of the furnace is the cylindrical hearth in which the molten products collect. There are two outlets from the hearth at different levels, the metal tap and the cinder notch. They are kept plugged, except when the metal or slag are being tapped from the furnace. Near the lower part of the bosh, water-jacketed pipes, tuyères, lead through the walls of the furnace to admit the blast of hot air supplied through the large pipe encircling the furnace. The solid charge is introduced through a charging hopper without undue loss of gaseous products. Each furnace is provided with a series of stoves, usually four, for preheating the air blast. They are arranged so that three are heated by the combustion of gas, while the fourth, previously heated, serves to heat the air blown through it.

The solid charge of the furnace consists of the proper proportions of ore, coke, and flux introduced in successive layers. The shaft of the furnace is kept filled to the stock line. Coke is the fuel and the source of carbon monoxide, the reducing agent. The flux, usually limestone, reacts with silica and complex silicates to form a fusible slag. All products of the furnace must be liquid or gaseous so that continuous operation may be maintained.

The materials in the charge, except coke, react to form products that melt at about 1400°, the temperature just above the tuyères. The solid coke, heated to incandescence as it burns in the blast of hot air, rests on the furnace floor and supports solids in the stack.

During the operation of the furnace, the solid charge settles at the rate of about 3 in. per minute. The hot air is delivered at a temperature of about 500° and a positive pressure of 15 lb. per square inch. The temperature varies from 1400° just above the tuyères to 200°
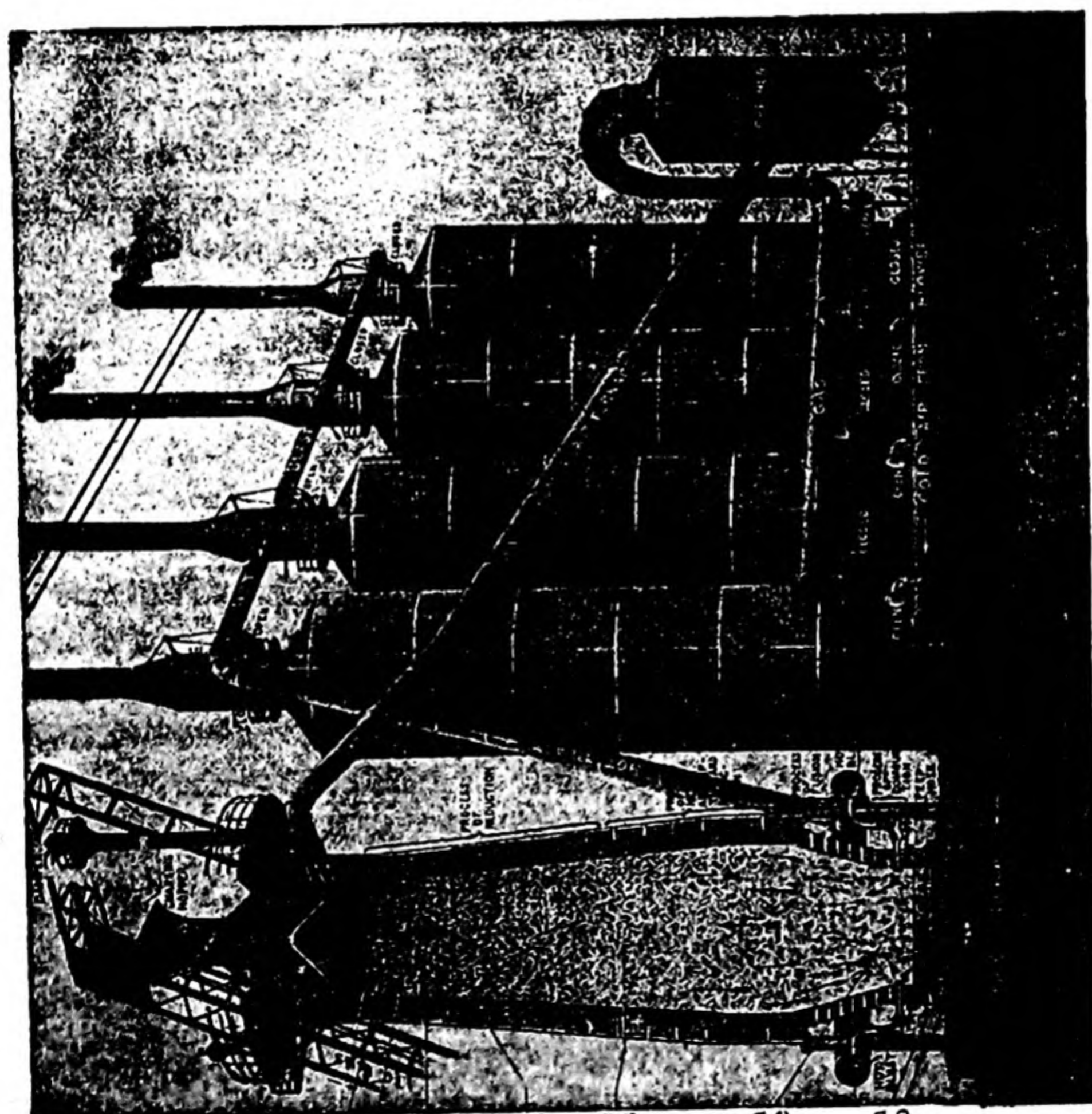
Coke
Ore
Limestone

300°

Reduction
Begins

Limestone
Decomposes

Maximum
Temperature

Cinder Notch
Metal Tap

*Fig. 130. Blast Furnace with Stoves.
(Courtesy of The Scientific American.
Copyright)*

at the top of the furnace. The reactions that take place in the furnace fall into four groups, *viz.*, the combustion of the fuel, the reduction of the ore, the formation of slag, and the formation of impurities which enter the metal. Coke burns to form carbon monoxide, releasing enough heat to maintain the temperatures necessary for the reactions.

$$2 C + O_2 \longrightarrow 2 CO + 52,860 \text{ cal.}$$
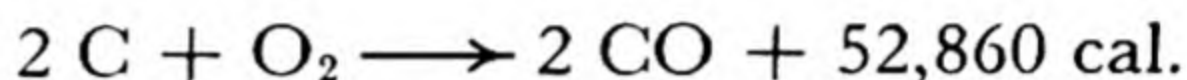
Carbon monoxide, rising through the charge, reduces iron oxide and is converted into carbon dioxide, and again reduced to the monoxide by the hot coke. At the lower temperatures near the top of the furnace, carbon monoxide is the more stable product.

The reduction of the ore commences in the upper part of the furnace. Ferric oxide is reduced to magnetic oxide of iron at 500°, about 10 ft. below the stock line.

$$3 Fe_2O_3 + CO \longrightarrow 2 Fe_3O_4 + CO_2$$
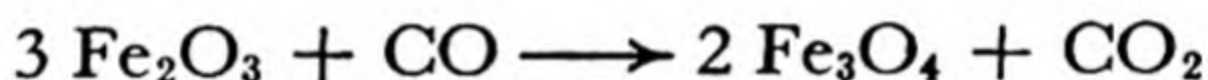
The magnetic oxide is reduced to ferrous oxide at 800–900°, about 20 ft. below the stock line.

$$Fe_3O_4 + CO \longrightarrow 3 FeO + CO_2$$
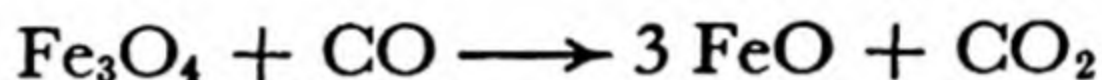
The reduction of ferrous oxide takes place at 1000°, about 40 ft. below the stock line. Iron reacts with hot carbon to form *cementite*, Fe_3C, thus lowering the melting point so that the metal melts at the temperature of the furnace, although the melting point of pure iron is 1535°. The liquid metal trickles down over the unburned coke and collects in the spaces between lumps of coke in the hearth.

Slag formation involves a number of complex reactions between impurities of an acidic nature and the basic flux. The principle may be illustrated by reactions of limestone and silica.

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$
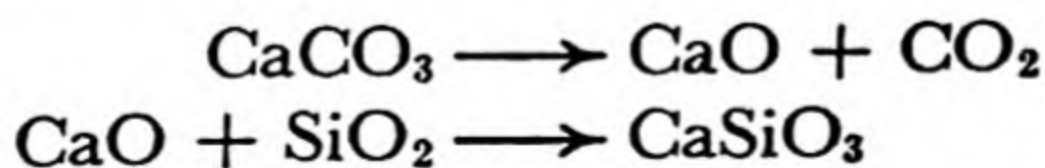
The specific gravity of the molten slag is about 2.5, and therefore it collects in a layer floating on the surface of the iron. Droplets of molten iron pass through the layer of slag. If the slag contains an excess of basic ingredients, reactions removing sulfur occur.

$$CaO + FeS + C \longrightarrow Fe + CO + CaS$$
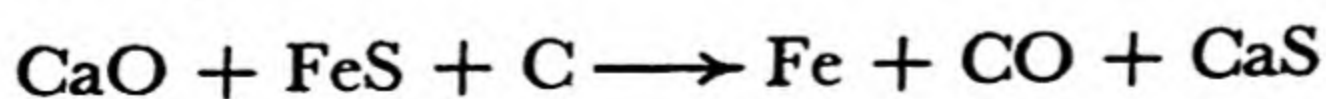
Phosphorus is probably present in the ore as phosphate. In the reducing mixture in the furnace phosphates are reduced to form phosphides. Similarly, silica may be reduced to form elementary silicon which then reacts with iron.

$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO$$
$$2\,Fe + Si \longrightarrow Fe_2Si$$
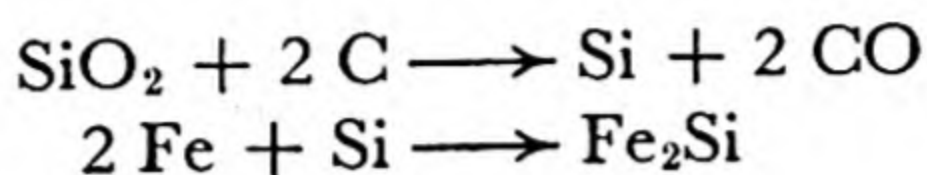
Sulfur does not usually occur in significant proportions in oxide ores, but is introduced in the organic matter with coke. Sulfur is volatilized from these compounds and combines with iron.

$$Fe + S \longrightarrow FeS$$
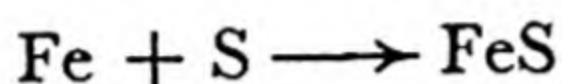
The binary compounds of iron with carbon, phosphorus, silicon, and sulfur dissolve in iron, whereas oxysalts do not. Approximately 75 per cent of the manganese enters the iron as metallic manganese.

The products of the blast furnace are pig iron, slag, and blast furnace gas. Molten iron is tapped from the furnace at four or five hour intervals and is either cast into pigs or transferred in the liquid condition to the steel furnaces. A modern blast furnace produces 1000 tons of pig iron daily. For this purpose approximately 2000 tons of ore, 900 tons of coke, and 400 tons of limestone are required. About 3000 tons of air are blown through the furnace. Approximately 500 tons of slag and 150,000,000 cu. ft. of blast furnace gas are formed. *Pig iron* varies in composition, but usually contains approximately 92–94 per cent of iron, 3.5–4.2 per cent of carbon, 1–3 per cent of silicon, 1–2 per cent of manganese, and fractions of 1 per cent of sulfur and phosphorus. Pig iron melts at temperatures ranging between 1150° and 1250°, depending on its composition. Pig iron is hard and brittle. It is coarsely crystalline and has little tensile strength. It is used in the production of wrought iron and steel, and in the manufacture of iron castings.

The slag is essentially a mixture of silicates containing small proportions of aluminates, phosphates, and sulfates. It has no important industrial uses. The solid may be crushed and used as ballast for railroads and for filling in embankments. Some grades of slag may be used in the production of cement.

Blast furnace gas contains approximately 25 per cent of carbon monoxide, 10–15 per cent of carbon dioxide, and 58–60 per cent of

nitrogen. Solid materials, carried along as dust, are removed and the gas is used as a fuel. Approximately one half of the gas is used to heat air and to operate the engines blowing the hot air into the furnaces. The remainder is used for general fuel purposes.

Cast Iron. Iron castings may be made directly from the blast furnace metal, but more frequently the iron is remelted. The composition of cast iron is in general the same as that of pig iron, though separation of slag and other small changes in composition may occur in the melting furnace. There are two commercial grades of cast iron. *White cast iron* is obtained by cooling the product quickly. Most of the carbon remains in combination with the iron as cementite, and the product is hard and brittle. *Gray cast iron* results from slow cooling of the iron. The carbide decomposes, and carbon
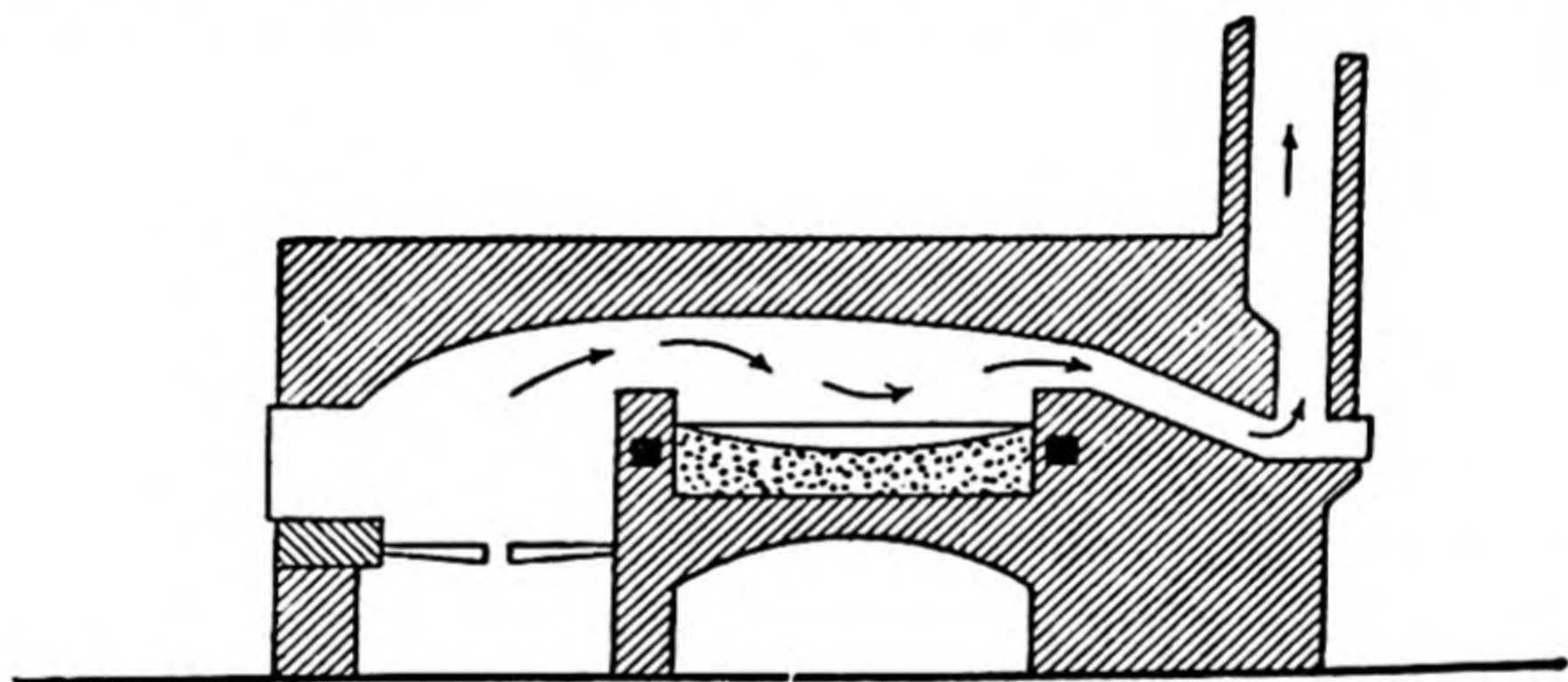
Fig. 131. Puddling Furnace

separates to a large extent to give flakes of graphite throughout the iron. This product is softer and stronger than the white variety. If castings made of white cast iron are heated for some time at temperatures of 800–900°, the iron carbide decomposes, and graphite remains in very finely divided particles throughout iron. This variety is known as *malleable cast iron*. Castings, such as parts of stoves, furnaces, and radiators, may be made directly from pig iron.

Wrought Iron. Wrought iron has two components, pure iron and slag. The percentage of slag may vary from a few tenths of 1 per cent to as much as 3 per cent, depending on the uses for which the product is intended. The slag is distributed throughout the iron in fine fibers and films. Wrought iron is usually made in a puddling furnace. (Fig. 131.) This furnace is a reverberatory furnace lined with blocks of hematite or magnetite. Pig iron is

charged into the hearth and melted by flames deflected from the low roof. Oxide ore is added when the iron has melted. Silicon and phosphorus are oxidized by ferric oxide, and the products react with additional iron oxide to form a slag consisting primarily of ferric phosphate and ferric and manganous silicates. Sulfur is taken into the slag primarily as the sulfide. The temperature is then raised, and the carbon is oxidized to form carbon monoxide. The charge is worked with iron rods, "puddled." As the impurities are oxidized, the melting point of iron rises and solidification commences with the formation of a pasty material. When the reactions are complete, the material is worked into large balls, "blooms," which are removed from the furnace and rolled to squeeze out the excess of slag and at the same time to disperse the desired proportions of slag in thin films throughout the iron.

Wrought iron is tough, malleable, and has high tensile strength. It can be welded and worked under the hammer. This material is used for chains, bolts, anchors, and wire fencing. Its high melting point makes it suitable for making grate bars. Wrought iron's chief value lies in its resistance to corrosion. This is attributed to the purity of the metal and to the presence of films of slag which prevent deep pitting of the product. Wrought iron is used in making pipes and tubing, plates, sheets, and bars. Soft steel made in open-hearth furnaces has replaced wrought iron for many uses.

Steel. Carbon steels are practically free from silicon, sulfur, and phosphorus. Mild steel contains up to about 0.2 per cent of carbon, medium steel, 0.2–0.6 per cent, and hard steel, 0.75–1.5 per cent. The two most important processes for the production of steel from pig iron are the open-hearth process and the Bessemer process. Electric furnaces are also used extensively in the production of steel, but they are generally charged with the partly refined product of the open-hearth furnace. About 90 per cent of the steel in the United States is made by the open-hearth process.

The Open-Hearth Process. This process provides for the removal of sulfur and phosphorus as well as silicon and carbon from pig iron and for the production of high-grade steel. The open-hearth furnace (Fig. 132) is a reverberatory furnace. The furnaces vary in size, but a common size is one with a hearth approximately 40 ft. long, 12 ft. wide, and 2 ft. deep. The lining of the hearth

in the basic process is usually magnesite or dolomite. The furnace is heated by the combustion of a fuel gas or oil in a blast of air. High temperatures are maintained by preheating the gases. This is done efficiently by the Siemens-Martin heat regenerating process. The entering gases are blown through a checker work of hot brick on one side of the furnace, and the hot gases emerging from the furnace pass through a similar checker work on the opposite side. The direction of the flow of gases is reversed at suitable intervals.

The charge consists of 50–100 tons of pig iron, a high grade iron oxide ore as the oxidizing agent, limestone as a flux, and scrap iron which dilutes the impurities in the pig iron and shortens the time of operation. Carbon monoxide escapes as a gas, and silicon, sulfur, and phosphorus are removed in the slag. The following equations are typical of the reactions involved.

$$3\ Fe_3C + Fe_2O_3 \longrightarrow 11\ Fe + 3\ CO$$
$$6\ Fe_3P + 5\ Fe_2O_3 \longrightarrow 28\ Fe + 3\ P_2O_5$$
$$P_2O_5 + 3\ CaO \longrightarrow Ca_3(PO_4)_2$$
$$3\ Fe_2Si + 2\ Fe_2O_3 \longrightarrow 10\ Fe + 3\ SiO_2$$
$$SiO_2 + CaO \longrightarrow CaSiO_3$$
$$FeS + CaO + C \longrightarrow Fe + CaS + CO$$
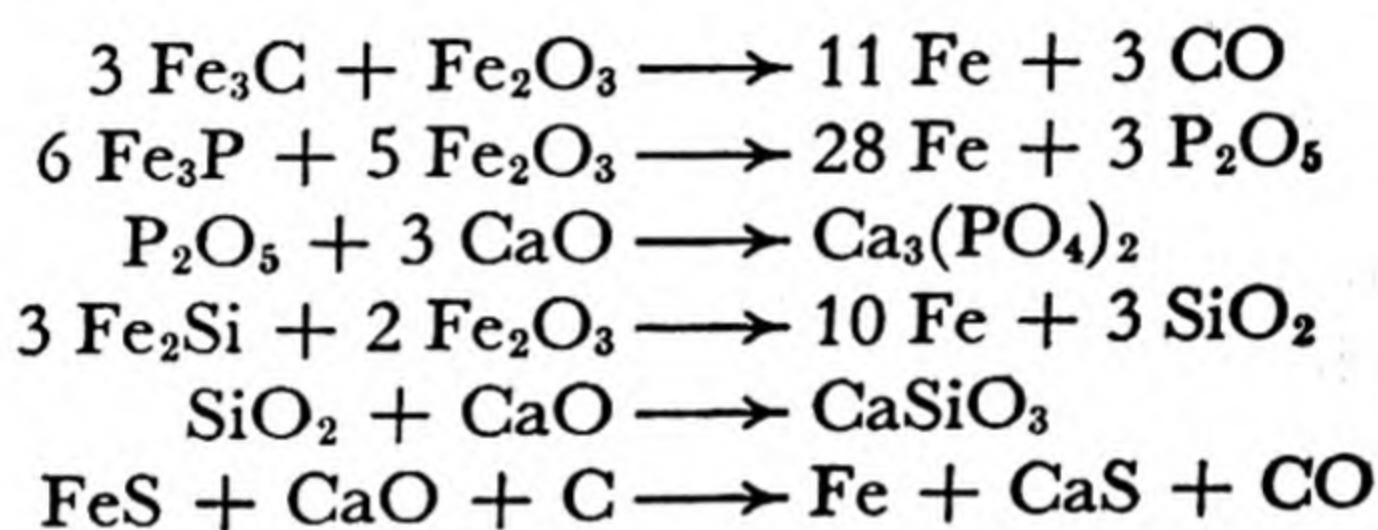
The process is completed in 5–8 hours for a 50 ton charge. The required percentage of carbon is now introduced by the addition of a high-carbon alloy, such as ferromanganese, which contains 5–7 per cent of carbon and up to 80 per cent of manganese. The product is tapped from the furnace into large ladles, and the slag is allowed to overflow into pots for its removal. Deoxidizers, known as *scavengers*, are added at the time of pouring to remove entrapped gases that would produce flaws and thus weaken the steel. Aluminum, titanium, and ferrosilicon are used for this purpose. The steel is then cast in ingot molds.

Open hearth steel is a high-grade product of uniform and specified composition. It is suitable for the manufacture of steel rails, bridge girders, machinery of different kinds, and other products that may be subject to sudden strains.

The Bessemer Process. A process for burning carbon out of pig iron by means of a blast of air was patented by Kelly, an American, in 1852. The patent rights were secured, and the process was per-
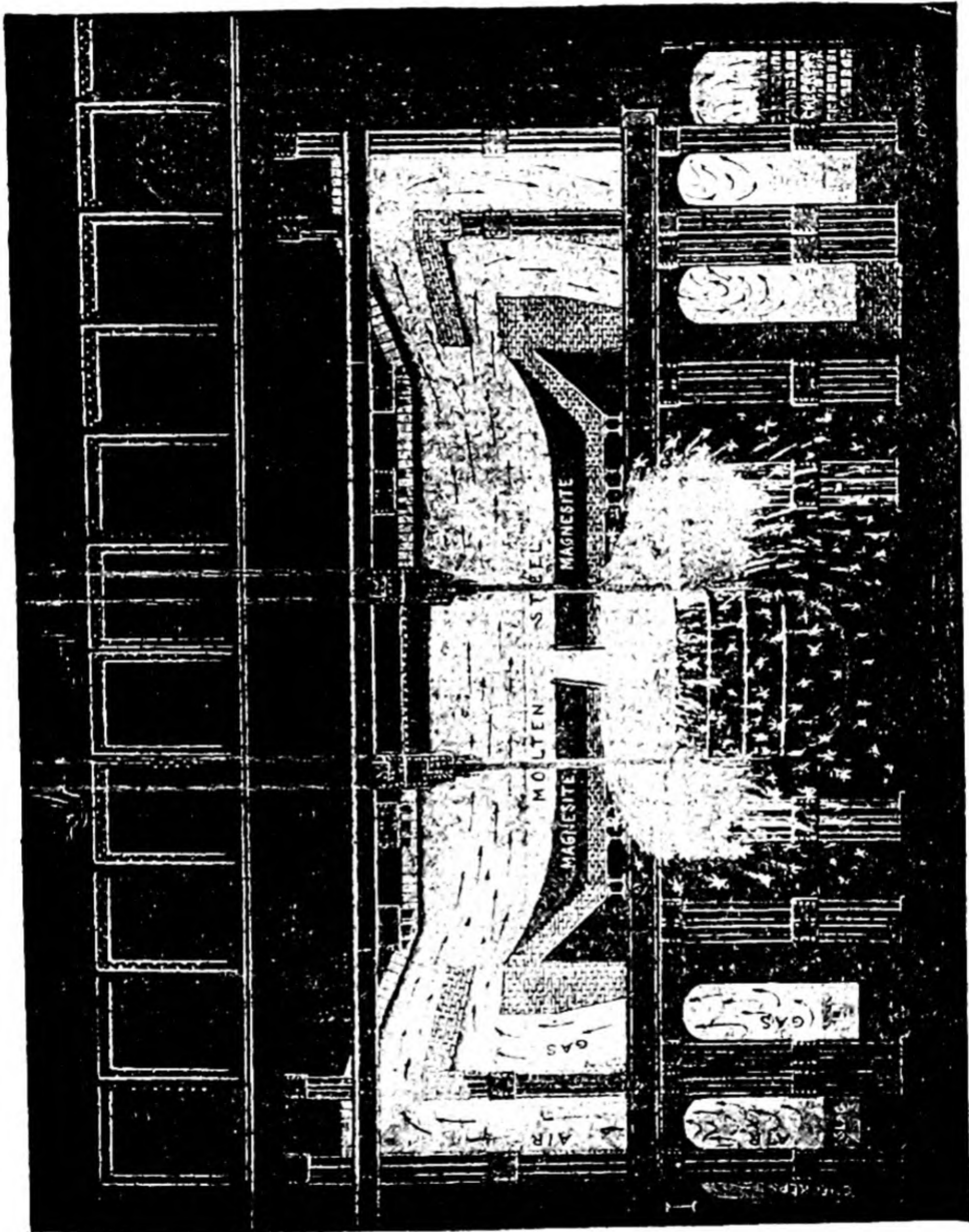
Fig. 132. Open-Hearth Furnace. (Courtesy of *The Scientific American.* Copyright)

fected by Bessemer, an Englishman, in 1855. The process is operated in a large converter made of steel and lined with silica and clay. The converter (Fig. 133) is mounted on trunnions, so that it may be tipped to any desired angle. The charge, consisting of about 15 tons of molten pig iron, is introduced when the converter is in a nearly horizontal position. The converter is brought to the upright position, and a blast of air is blown through the charge, the blast being admitted through a number of channels in the bottom of the converter. Carbon is oxidized to carbon monoxide which burns at the mouth of the converter. Silica unites with some of the oxidized iron to form a slag. When the flame of burning carbon monoxide dies away, the converter is turned back to the horizontal position, cutting off the air blast, and a required amount of high-carbon alloy is added. Scavengers are also introduced to remove entrapped gases and to reduce oxidized products. The reactions are completed in fifteen to twenty minutes. With the acidic lining of silica, the converter does not effect removal of sulfur and phosphorus, and is limited to the treatment of pig iron from ores which contain only very small percentages of these elements. It is possible to employ a lining of basic material for the Bessemer converter but the basic Bessemer process has not been extensively used in American practice. Bessemer steel is subject to defects due to incomplete removal of objectionable materials and to lack of uniformity.

A *duplex process*, involving the use of both the acid Bessemer process and the basic open-hearth process, is used at some plants. After the rapid removal of silicon, and most of the carbon, in a Bessemer converter, the molten metal is transferred to an open-hearth furnace, where the removal of phosphorus and the finishing of the product may be accomplished quickly.

Electric Furnace Steel. The high-grade steel required for automobile engines, axles, and wheels, and for airplane parts and tool steel, must have as exact and uniform composition as practicable. Large quantities of alloy steels are produced in the electric arc furnace. This furnace has a basic lining, and the removal of impurities is accomplished the same way as in the open-hearth process. The electric furnace has the advantage over the open-hearth that higher temperatures can be maintained, and that there are no combustion gases causing contamination. The charge of the electric
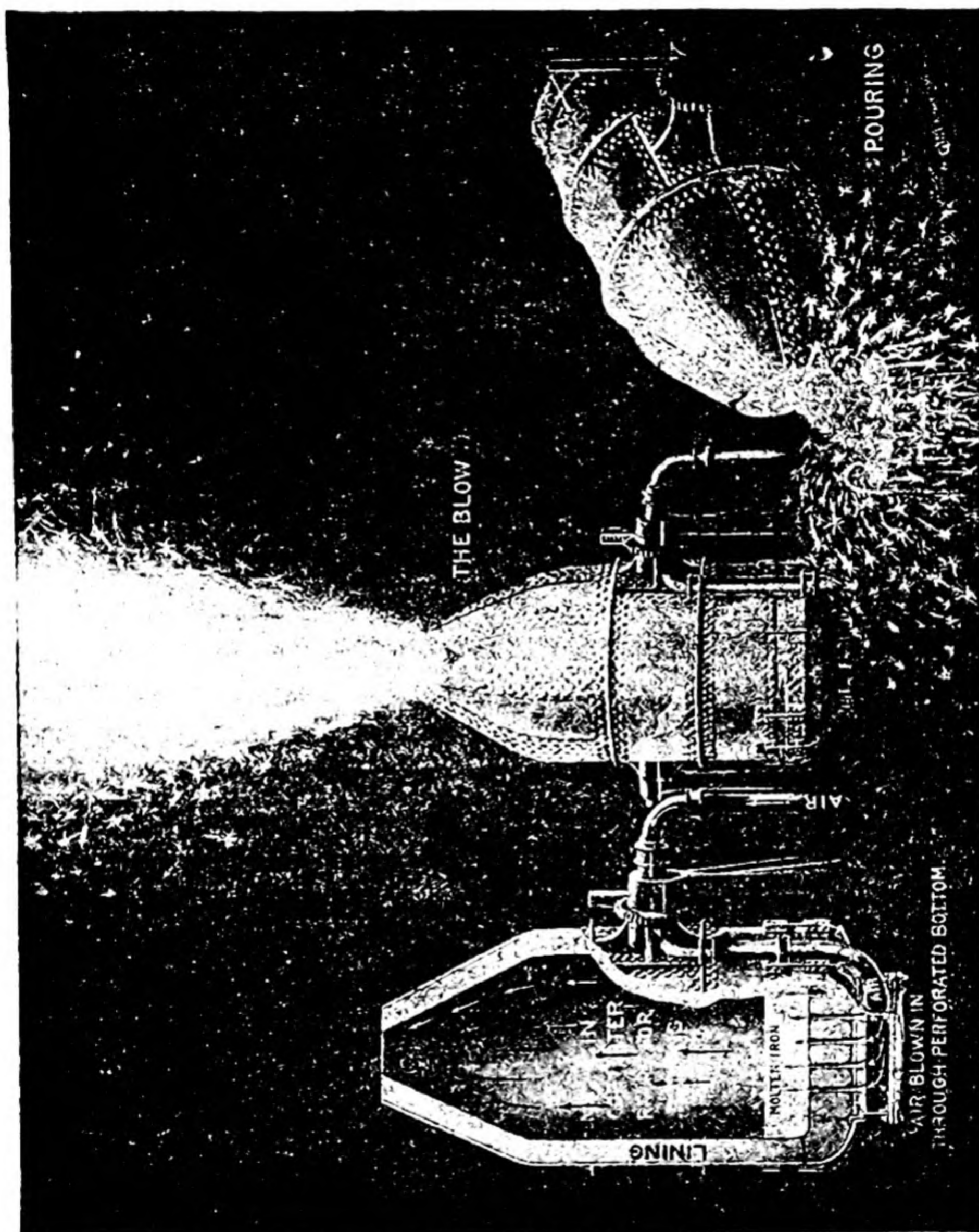
Fig. 133. Bessemer Converter. (Courtesy of *The Scientific American.* Copyright)

furnace is usually the open-hearth product. The operations in this furnace remove phosphorus, sulfur, and oxygen. The removal of phosphorus is accomplished through the use of iron oxide and lime with fluorspar, making a fluid slag. After this step is complete, the slag is skimmed off, and lime and powdered coke are added to remove sulfur. Specific quantities of carbon or alloying metals are added to produce the finished product.

Crucible Steel. A small quantity of high-carbon steel is made from wrought iron in a crucible process. It is used for the manufacture of razors, watch springs, and other articles for which the specifications are rigid. Small quantities, 60–100 lb., are produced in a batch by heating wrought iron with the required amount of carbon in crucibles made of graphite and clay. Steel for such uses is now produced principally in electric furnaces.

The Tempering of Steel. The iron-carbon system is very complex. Cementite, Fe_3C, may exist in solid solution in iron or mixed with iron, or it may be partly in the one condition and partly in the other. The size of the particles may vary, and there are several forms of iron that are stable at different temperatures. If the per cent of carbon in the metal is above 1.7, free carbon may separate in the form of graphite, producing gray cast iron. At temperatures above 900–1000°, depending on the composition, the carbon is entirely in solid solution in γ-iron, unless the proportion of carbon is above 1.7 per cent. This product is known as *austenite*. If austenite containing less than 0.9 per cent of carbon is cooled slowly so that equilibrium is attained, α-iron or β-iron separates until the eutectic point (see page 436) is reached at 690°. If the per cent of carbon is above 0.9, cementite separates from the solid solution during cooling to the eutectic point. Cementite and α-iron separate together at 690°, the eutectic point, to form the eutectic mixture known as *pearlite*, and the decomposition of the solid solution is completed. This product is composed of cementite particles embedded in pure iron, and is soft steel. Sudden cooling does not allow time to reach equilibrium, and the transitions do not occur at low temperatures. In this way, the solid solution, austenite, may be obtained at room temperature, giving a hard product, if the percentage of carbon is great enough. If now the hardened steel is reheated to some definite intermediate temperature, separa-

tion into iron and cementite commences. The extent of this separation depends on the temperature and the length of time allowed before quenching it to arrest further changes. In a tempered steel, a portion of the carbon is combined in the form of cementite particles while the remainder is in solid solution in iron. The properties of steel depend not only on the percentage of carbon but also on the proportions of carbon in the carbide and in solid solution. Other factors that influence the properties are the size and shape of the grains and the strains set up in the material.

Case-Hardened Steel. In the manufacture of certain articles, such as machine parts, it is often desirable to produce a product with the hard surface of a high-carbon steel, retaining the toughness of a low-carbon steel throughout the body of the metal. This may be accomplished by manufacturing the article from low-carbon steel and then baking it, packed in carbon or in a cyanide, at 850–900°, until the desired proportions of carbon have been absorbed into the surface of the metal. Steel containing approximately 1 per cent of aluminum, 1.5 per cent of chromium, and 0.2 per cent of molybdenum may be hardened by a *nitriding process*. The articles are heat-treated and then placed in a container to be heated at about 500° in an atmosphere of ammonia. The decomposition of ammonia produces nitrogen which combines with the alloying metals in the surface of the steel, forming nitrides. This process gives a greater degree of surface hardening than any other.

Alloy Steels. Steels containing other metals alloyed with iron are called alloy steels. The metals most extensively used in alloy steels are nickel, manganese, chromium, vanadium, tungsten, molybdenum, and silicon. Some of the alloy steels contain carbon, while others do not contain appreciable quantities of this substance. Steels containing relatively large proportions of the alloying metals are usually prepared in electric furnaces, and those containing relatively small proportions in the open-hearth furnace. Machine parts made from certain alloy steels are lighter and stronger than when made of carbon steel. This is especially important in the automobile and aircraft industry and in transportation vehicles in general.

The alloying metals improve the properties of the carbon steels in some instances and impart special properties in others. *Nickel steel*, containing 3.25 per cent of nickel and 0.2–0.5 per cent of

carbon, has high elastic limit and ductility. It is used for structural purposes. Some nickel alloys, such as Invar, containing about 35 per cent of nickel, have low coefficients of expansion. *Manganese steel*, containing 12–13 per cent of manganese and 0.9–2 per cent of carbon, is very tough when properly heat-treated. It is used in railroads on "frogs" and "cross-overs," in steam shovel buckets, and in rock-crushing machinery. *Chrome steel*, with 0.5–2 per cent of chromium, is very hard and has high tensile strength. It is suitable for making dies, files, ore stamps, and ball bearings. *Stainless steel*, with 10–15 per cent of chromium and about 0.3 per cent of carbon, is used in the manufacture of cutlery, valves, turbine parts, and in structural materials used in many chemical processes. *Chrome-nickel steel*, containing 4 per cent of nickel, 2 per cent of chromium, and 0.33 per cent of carbon, is used for making armor plate and armor-piercing projectiles. *Chrome-vanadium steel*, with 0.7–1.4 per cent of chromium and 0.14–0.25 per cent of vanadium, has high tensile strength and resistance to stresses. This steel finds extensive application in automobile axles and springs. Alloy steels containing *molybdenum* are now used instead of chrome-vanadium steel for many purposes. *Tungsten steel* is used primarily for the manufacture of tools. Carbon steel is not suitable for high-speed lathe tools, because the heat, generated by friction, causes a change in the composition of carbon steel with consequent loss of temper. Tools made of an alloy containing about 18 per cent of tungsten, 5 per cent of chromium, 0.3 per cent of vanadium, and 0.7 per cent of carbon, may be heated red hot without loss of temper. *Silicon steel*, about 2.75 per cent of silicon, has a special use in electrical transformers and in magnet cores. *Duriron*, with about 16 per cent of silicon, is highly resistant to acid corrosion. The iron alloy known as *Allegheny metal* contains 17–20 per cent of chromium, 7–10 per cent of nickel, and 0.5 per cent each of carbon and manganese. It has high resistance to corrosion. *An alloy cast iron*, containing 3.3 per cent of carbon, 2.3 per cent of silicon, 0.75 per cent of manganese, and 0.7 per cent of nickel, is used for automobile blocks.

The Ferroalloys. The ferroalloys are alloys of iron with one or more other elements, containing larger percentages of the alloy metal than the alloy steels. Some of the ferroalloys are used in the iron industry as deoxidizing agents for the removal of entrapped

gases. In other instances, ferroalloys are introduced to supply the required proportions of the alloying metal. The ferroalloys are produced by the reduction of an iron oxide ore and the oxidized ore of the alloying metal.

Compounds of Iron. The common ions of this metal are the ferrous ion, Fe^{++}, and the ferric ion, Fe^{+++}. Ferrous compounds are formed by the mild oxidation of the metal, as by reaction with hydrogen ions, and also by the reduction of ferric ions.

$$Fe + 2\,H^+ \longrightarrow H_2 + Fe^{++}$$
$$2\,Fe^{+++} + S^{--} \longrightarrow 2\,Fe^{++} + S$$
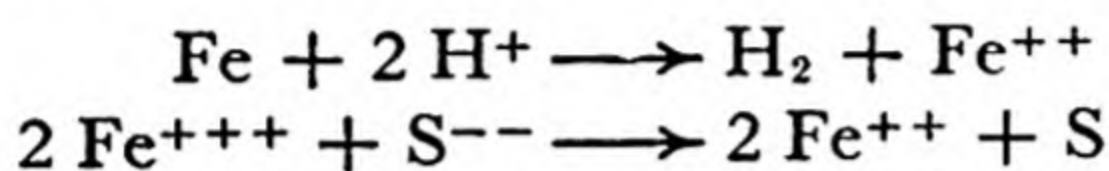
Ferric ions are formed by the oxidation of ferrous ions and by the strong oxidation of the metal, as with chlorine.

$$4\,H^+ + NO_3^- + 3\,Fe^{++} \longrightarrow NO + 3\,Fe^{+++} + 2\,H_2O$$
$$Fe + 3\,Cl_2 \longrightarrow 2\,FeCl_3$$
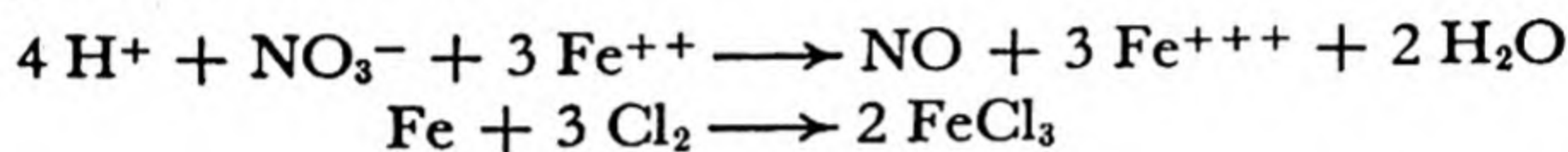
The sulfates and chlorides are the most familiar salts of iron. These ions hydrolyze to form acidic solution.

$$Fe^{++} + H_2O \rightleftharpoons Fe(OH)^+ + H^+$$
$$Fe^{+++} + H_2O \rightleftharpoons Fe(OH)^{++} + H^+$$
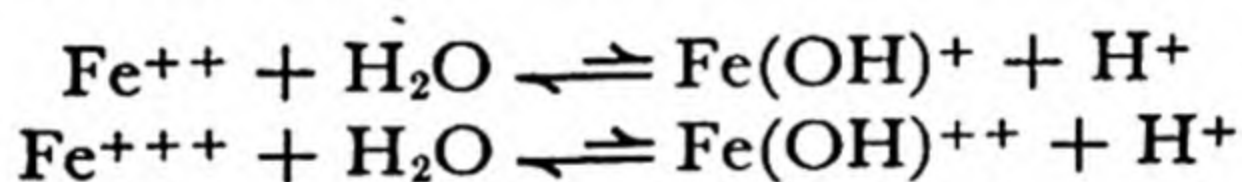
Ferric ions are more strongly acidic than ferrous ions.

Oxides and Hydroxides of Iron. Iron yields two simple oxides, *ferrous oxide*, FeO, and *ferric oxide*, Fe_2O_3. A third compound, commonly called *magnetic oxide of iron*, Fe_3O_4, is best represented by the formula $Fe(FeO_2)_2$, ferrous metaferrite. Ferrous oxide and hydroxide are basic in properties. Ferrous oxide may be prepared by heating ferrous oxalate.

$$FeC_2O_4 \longrightarrow FeO + CO + CO_2$$

When heated in air, this oxide burns, forming ferric oxide. Ferrous hydroxide is precipitated by the reaction of a soluble basic hydroxide with ferrous salt solutions. The pure compound is white but rapidly darkens in air, forming first a green product and finally the reddish brown ferric hydroxide. Ferrous solutions contain enough ferric iron to give the green product at once, unless special precautions are taken to reduce the iron completely to the ferrous state and to exclude oxygen.

Ferric oxide occurs naturally in the hematite ore. The pure oxide may be prepared by heating ferrous oxide and hydroxide in air. Ferric hydroxide, the hydrated oxide of ferric iron, $Fe_2O_3(H_2O)_x$, is precipitated by the reaction of soluble ferric salts with bases.

Chlorides of Iron. *Ferrous chloride*, **$FeCl_2$,** as stated earlier, is formed in solution by the reaction of iron with hydrochloric acid and by reducing ferric chloride in acidic solution by such agents as metallic iron, stannous chloride, or hydrogen sulfide.

Ferric chloride, **$FeCl_3$,** is the most common ferric salt. Usually, it is prepared by the reaction of hydrochloric acid with the oxide and by oxidation of ferrous chloride.

Sulfates of Iron. *Ferrous sulfate*, **$FeSO_4$,** the most important ferrous salt, is a by-product of the "pickling" of iron to be galvanized or tinned. The hydrate, $FeSO_4(H_2O)_7$, crystallizes from concentrated aqueous solutions. This substance is known as *green vitriol* and as *copperas*. Ferrous sulfate is used as a disinfectant, in dyeing, in water purification, and in the preparation of ink. The addition of ferrous sulfate to an extract of nut-galls yields ferrous tannate. Ferrous tannate is soluble and colorless, but it is oxidized by air to form ferric tannate which is insoluble and black. A dye is added to the ferrous tannate solution to make writing visible from the first. Ink stains from this variety of ink can be washed out only by first reducing the iron compound. This may be accomplished by soaking the material with the ink spot in an ammonium oxalate solution. Of course, this method cannot be used if the ammonium oxalate will damage the fabric or affect the color of the dyes.

When a solution containing equimolar amounts of ferrous sulfate and ammonium sulfate is evaporated to the point of crystallization, a double salt, *Mohr's salt*, $(NH_4)_2SO_4FeSO_4(H_2O)_6$, is deposited in the form of pale green crystals. This salt is more stable toward oxidation than other ferrous salts, so that it is used as the common laboratory reagent to supply ferrous ions.

Ferric sulfate, **$Fe_2(SO_4)_3$,** is formed by the oxidation of ferrous sulfate in a solution containing free sulfuric acid. Like aluminum and chromic ions, it yields alums such as the potassium iron alum, $KFe(SO_4)_2(H_2O)_{12}$.

Complex Cyanides of Iron. Both ferrous and ferric iron yield complex cyanide ions, *ferrocyanide*, $Fe(CN)_6^{----}$, and *ferricyanide*,

$Fe(CN)_6^{---}$, respectively. Potassium cyanide reacts with solutions of ferrous salts with the precipitation of ferrous cyanide. This salt dissolves in an excess of the cyanide, forming ferrocyanide.

$$Fe^{++} + 2\ CN^- \longrightarrow Fe(CN)_2 \downarrow$$
$$Fe(CN)_2 + 4\ CN^- \longrightarrow Fe(CN)_6^{----}$$
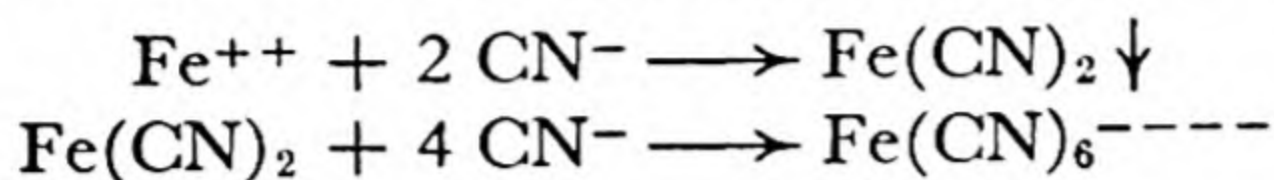
The ferrocyanides of sodium and potassium are usually prepared as by-products in the manufacture of coke. A portion of the combined nitrogen in coal is evolved as hydrogen cyanide. When the gas is passed over iron oxide, hydrogen cyanide is absorbed with the formation of iron cyanide. By reaction with lime, this is converted into calcium ferrocyanide, from which the ferrocyanides of sodium and potassium may be obtained. Ferrocyanides may be oxidized to ferricyanides by chlorine.

$$2\ Fe(CN)_6^{----} + Cl_2 \longrightarrow 2\ Fe(CN)_6^{---} + 2\ Cl^-$$
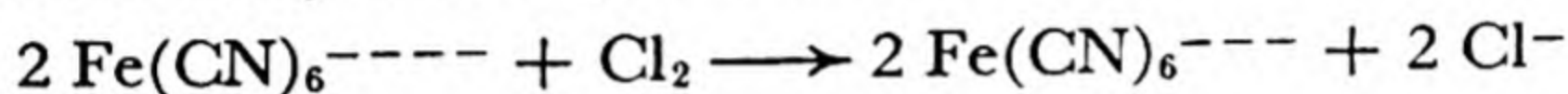
Potassium ferricyanide is now commonly prepared by the electrolytic oxidation of the ferrocyanide at the anode.

$$Fe(CN)_6^{----} - 1\ \epsilon \longrightarrow Fe(CN)_6^{---}$$
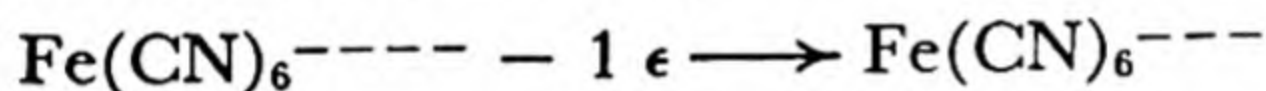
Soluble ferrocyanides react with ferric iron to form the slightly soluble *Prussian blue*, $Fe_4[Fe(CN)_6]_3$. With ferrous iron, the ferrocyanides form a white precipitate of potassium ferrous ferrocyanide, $K_2Fe[Fe(CN)_6]$. A ferricyanide solution mixed with a ferric salt gives a dark brown solution containing undissociated ferric ferricyanide, $Fe[Fe(CN)_6]$, and with ferrous iron, the ferricyanide gives a dark blue precipitate, Turnbull's blue, commonly called ferrous ferricyanide. Both Turnbull's blue and Prussian blue appear to have the same composition, indicating that an oxidation-reduction reaction takes place when the solutions are mixed.

COBALT AND NICKEL

Cobalt occurs in *cobaltite*, CoAsS, and in *smaltite*, CoAs$_2$. The arsenide ores in Ontario also contain iron, nickel, copper, and silver. The most important source of nickel is the mineral *pentlandite*, NiS(FeS)$_2$, which occurs with additional iron sulfide and copper sulfide in the Sudbury deposits.

Production of Cobalt and Nickel. The production of these metals requires a number of steps that will be indicated but not

described in detail. *For the production of cobalt*, the arsenide ore is smelted in a small blast furnace, with the separation of crude silver if the ore is rich in this metal, and the formation of speiss and slag. The speiss consists primarily of arsenides of cobalt and nickel and contains also a matte of copper and iron sulfides and the remainder of the silver. The speiss is crushed, mixed with sodium chloride, and roasted in a reverberatory furnace. The product is leached with water, and a solution containing the chlorides of copper, cobalt, and nickel is obtained. Copper is displaced from this solution by scrap iron. The hydroxides of cobalt and nickel are precipitated, heated to remove water, and reduced to form the metals. Nickel may be separated from cobalt by heating the metal product at 50–100° in a current of carbon monoxide, with the formation of the volatile product *nickel carbonyl*, $Ni(CO)_4$. This compound is decomposed at 180° to form nickel.

For the production of nickel from the complex sulfide ores which contain approximately 4 per cent of nickel, the ore is first roasted to burn out a portion of the sulfur. The roasted ore is then smelted with a flux in a blast furnace, producing a matte containing nickel, copper, and iron. The matte is oxidized in a converter, as in the metallurgy of copper (see page 485) with silica as a flux. Most of the iron is removed in the slag, and a matte composed primarily of sulfides of nickel and copper is obtained. *Monel metal*, an alloy of nickel and copper containing about 67 per cent of nickel and 28 per cent of copper, may be formed by roasting the matte and reducing the oxides with carbon in a reverberatory furnace. Nickel may be produced from the nickel-copper matte by the Orford process. The matte is fused with carbon and sodium sulfate, and two layers are formed. Most of the nickel is in the bottom layer as nickel sulfide. This sulfide is oxidized to form the oxide which is then reduced with carbon in an open hearth furnace. The crude product is refined electrolytically with nickel sulfate as the electrolyte. Platinum is obtained as a by-product from the material that fails to go into solution at the anode during the refining.

Uses of Cobalt and Nickel. *Cobalt* is used in the production of alloys such as *stellite*, which contains cobalt and one or more of the following metals: chromium, tungsten, molybdenum, iron, and nickel. The proportions of the metals in this alloy may vary greatly.

One of the stellite alloys contains approximately 60 per cent of cobalt, 15 per cent of chromium, 20 per cent of tungsten, and 5 per cent of molybdenum, while another contains 30 per cent of cobalt, 4 per cent of chromium, 14 per cent of tungsten, and 52 per cent of iron. These alloys are used in high-speed lathes and also in surgical instruments to permit heating for sterilization without injury to the instrument. Cobalt is also employed in special steels for magnets.

Nickel is used extensively in the production of nickel steel and other alloys. Monel metal and nickel silver have been discussed previously on page 489. Nickel coins contain 25 per cent of nickel and 75 per cent of copper. To conserve nickel these coins are now made from an alloy of copper, silver, and manganese. *Nichrome*, 60 per cent of nickel, 15 per cent of chromium, and 25 per cent of iron, is employed in the manufacture of the heating elements for electric irons, toasters, ovens, and stoves. *Constantan*, 60 per cent of copper and 40 per cent of nickel, is also used in thermoelements. *Illium*, an acid resistant alloy, contains 62 per cent of nickel, 7 per cent of copper, 22 per cent of chromium, 8 per cent of molybdenum, and 1 per cent of iron.

Compounds of Cobalt. Cobalt yields ions in two oxidation states, cobaltous, Co^{++}, and cobaltic, Co^{+++}. *Cobaltous chloride*, $CoCl_2$, and *cobaltous nitrate*, $Co(NO_3)_2$, are the common soluble cobalt salts. They are prepared by the reaction of the oxide or hydroxide with the acids. Solutions of cobaltous salts are pink, and the crystalline salts, $CoCl_2(H_2O)_6$, and cobaltous nitrate, $Co(NO_3)_2(H_2O)_6$, are rose colored. The anhydrous solids and solutions of the salts in alcohol, containing only small proportions of water, are blue. *Cobaltous hydroxide*, $Co(OH)_2$, is precipitated by the addition of soluble basic hydroxides to solutions containing cobaltous ions.

$$Co^{++} + 2\,OH^- \rightleftharpoons Co(OH)_2 \downarrow$$
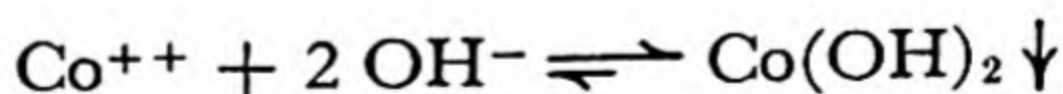
The precipitate darkens in air, due to oxidation.

$$4\,Co(OH)_2 + O_2 + 2\,H_2O \longrightarrow 4\,Co(OH)_3$$
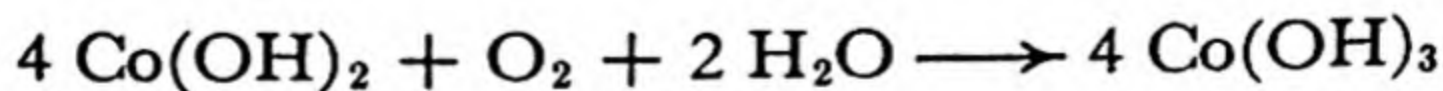
Cobaltous sulfide and carbonate may be prepared by precipitation. The cobaltous ion yields a number of *complex ions*, e.g., with ammonia, $Co(NH_3)_6^{++}$, with cyanide, $Co(CN)_6^{----}$, and with chlo-

ride, $CoCl_4^{--}$. Simple cobaltic salts are unstable toward reduction, but there are a number of complex cobaltic ions. The cobalti-cyanide ion, $Co(CN)_6^{---}$, is very stable, yielding a number of insoluble salts analogous to the ferricyanides. *Sodium cobaltinitrite* may be prepared by the reaction of a cobaltous salt with sodium nitrite and acetic acid.

$$NO_2^- + HC_2H_3O_2 \rightleftharpoons HNO_2 + C_2H_3O_2^-$$
$$Co^{++} + 5\,NO_2^- + 2\,HNO_2 \rightleftharpoons Co(NO_2)_6^{---} + NO + H_2O$$
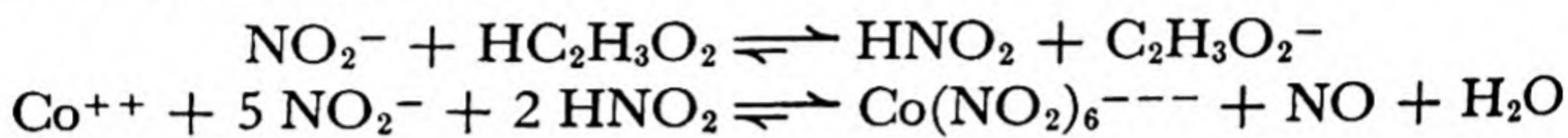
This ion is decomposed by an excess of a strong base with the pre-cipitation of cobalt hydroxide, and by strong acids with the evolu-tion of oxides of nitrogen. The ammonium and potassium salts are yellow crystalline solids with low solubility.

Compounds of Nickel. Nickel has an oxidation number of $2+$ in most of its compounds. No nickelic salts are known, but the metal yields a dioxide. The *sulfate* and *chloride* are the common nickel salts. They are prepared by the reaction of the acids with nickel oxide, NiO. The hydrated ions in solution are green, and the crystalline salts, $NiSO_4(H_2O)_7$ and $NiCl_2(H_2O)_6$, are green solids. Nickel also yields *complex ions* with ammonia, $Ni(NH_3)_6^{++}$, and with cyanide, $Ni(CN)_4^{--}$. *Nickel hydroxide* is formed as a light green, gelatinous precipitate by the addition of a soluble basic hydroxide to nickel salt solution.

$$Ni^{++} + 2\,OH^- \rightleftharpoons Ni(OH)_2 \downarrow$$
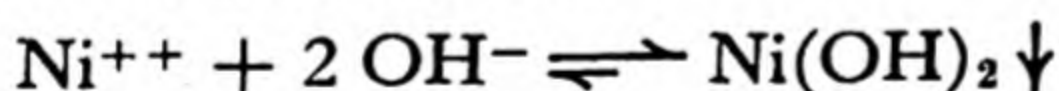
Nickel hydroxide suspended in basic solution may be oxidized by hypobromites to form *nickel dioxide*.

$$Ni(OH)_2 + BrO^- \longrightarrow NiO_2 + Br^- + H_2O$$
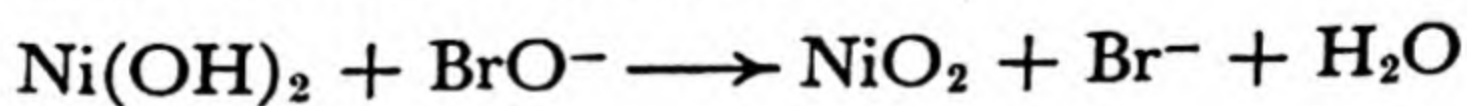
The Edison storage cell is based on a reversible oxidation-reduction between nickel dioxide and finely divided iron in contact with a basic solution. One electrode in the charged cell is coated with finely divided iron and the other with nickel dioxide. The elec-trolyte is a 21 per cent solution of potassium hydroxide. Iron is oxidized during the discharge of the cell, with the formation of ferrous hydroxide, and the iron electrode becomes negatively charged. Nickel dioxide is reduced to nickel hydroxide, developing a positive electrode potential. Different equations have been pro-posed to represent the reactions occurring in this cell, but the essen-

tial changes are shown by the following partial equations for the half reactions at the electrodes.

$$Fe + 2 OH^- \longrightarrow Fe(OH)_2 + 2 \epsilon$$
$$2 \epsilon + NiO_2 + 2 H_2O \longrightarrow Ni(OH)_2 + 2 OH^-$$
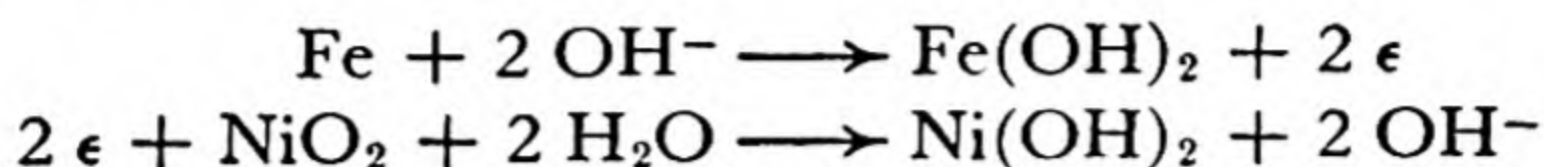
These products adhere to the electrodes, and the reactions of opposite effect occur during the charging of the cell. The operating voltage of the charged cell averages about 1.2 volts at 25°.

EXERCISES

1. What process is used for reduction of iron oxide ores? Describe the furnace.
2. What is the charge fed into the furnace and what is the function of each ingredient in this charge?
3. Show by equations the typical reactions involved in (a) liberation of the metal; (b) formation of slag; (c) source of impurities in the metal product.
4. Describe the composition and state uses of the products of the blast furnace.
5. What is the first step in refining pig iron to produce a more valuable product?
6. Show how the removal of impurities is accomplished in the reverberatory type of furnace provided with a basic lining.
7. How are impurities removed in the Bessemer converter with an acidic lining?
8. Which of these methods yields the better product? Explain.
9. After the removal of impurities, what is done to form steel?
10. What advantage has the electric furnace process over the open-hearth process in the production of steel?
11. What is meant by the tempering of steel? What are some of the changes brought about by the tempering of steel?
12. What are alloy steels? Give examples, with composition, properties, and uses.
13. Name the common alloying metals used in the steel industry. In what form are these introduced in the production of alloy steels?
14. How are the ferroalloys commonly prepared?
15. How are ferrous salts produced from iron? from ferric salts?
16. How are ferric salts commonly formed?
17. What similarities are noted in the compounds of iron, cobalt, and nickel? what differences?

SUPPLEMENTARY READINGS

Hayward, C. R., *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1929, chap. XXII.

Sneed, M. C., and J. I. Maynard, *General Inorganic Chemistry*, D. Van Nostrand Company, Inc., New York, 1942, chap. 45.

Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940, chap. XIX.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 47, 48.

Chapter 34

HYDROCARBONS

The extent to which carbon links atom to atom in the construction of complex molecules makes it unique among the elements. This property is shown to a much lesser degree by some of the other elements, *e.g.*, oxygen in peroxycompounds, silicon in a series of hydrides and related products, and boron in the hydroborons. The linking of atoms of carbon to one another makes possible the formation of a large number of compounds containing this element and a few others, such as hydrogen, oxygen, nitrogen, sulfur, and phosphorus. These substances are known as *organic compounds*. There are thousands of compounds containing only the two elements, carbon and hydrogen. These compounds are called *hydrocarbons*. Hydrocarbons occur in natural gas, petroleum, and coal. Many other hydrocarbons, not found among natural substances, are produced by synthetic processes.

The hydrocarbons are classified into a number of series, on the basis of the proportions of carbon and hydrogen they contain and the properties they exhibit. In each of these series there is a constant difference between each member and the one immediately preceding or following. Such a series of compounds is an *homologous series*, and the members are *homologues* of each other. A few members of several series of hydrocarbons are discussed in this chapter, but there are a great number of additional members in each series, and other series which are not touched upon.

Structural Isomers. There are numerous instances among the organic compounds in which two or more substances have the same molecular formula, *i.e.*, they have the same composition and molecular weight. In 1828, Wöhler discovered that the organic product, urea, may be produced by heating the salt, ammonium cyanate. These two substances may be represented by the same formula, N_2H_4CO, but it is customary to use different formulas, *viz.*, am-

monium cyanate, NH_4CNO, and urea, $(NH_2)_2CO$. The equation for the reaction in this conversion is:

$$NH_4CNO \longrightarrow (NH_2)_2CO$$
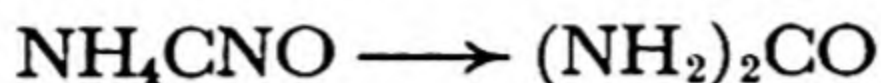
Before this discovery, it had been supposed that a specific composition and formula could represent only one substance. Two compounds having the same composition and molecular weight are known as *isomers*, and the phenomenon is called *isomerism*. There are nine hydrocarbons having the molecular formula, C_7H_{16}, and it is calculated that 336,319 isomers with the composition shown by the formula $C_{20}H_{42}$ are possible. The existence of isomers shows that the chemical nature of a substance depends not only on its composition but also on its constitution, *i.e.*, on the arrangement of the atoms with respect to each other and on the forces with which they are bound in the molecules. Compounds exhibiting differences in properties, due entirely to differences in constitution, are known as structural isomers.

Structural Formulas. The theory representing the constitution of organic molecules assumes that carbon has a covalence of four in all such compounds and that carbon atoms may be attached to other carbon atoms by electron sharing. On the basis of these two assumptions, electronic formulas to represent methane, ethane, and propane are:
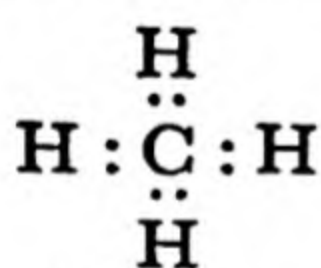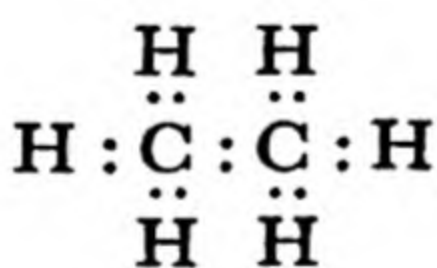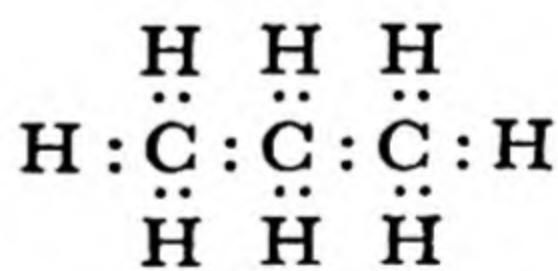
Structural or graphic formulas are written by using a line, called a valence bond, to represent each unit of covalence due to an electron pair.
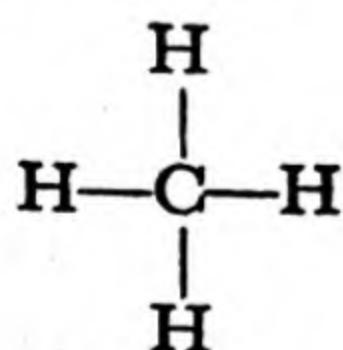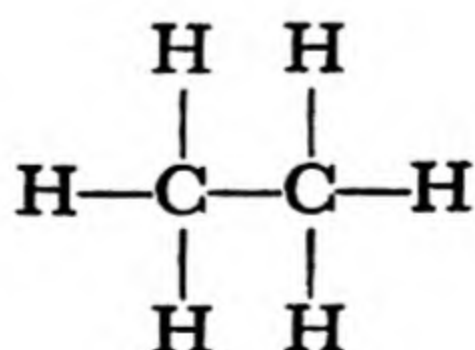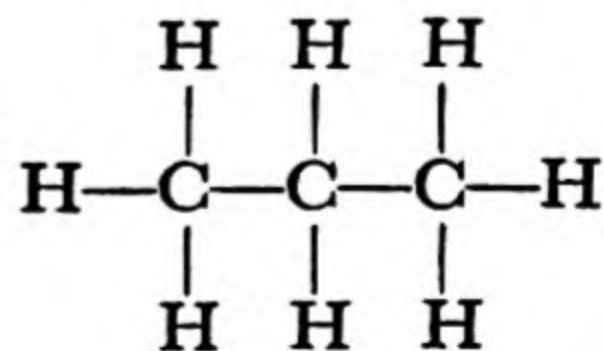
Valence bonds do not necessarily represent the oxidation number of carbon in its compounds, and graphic formulas do not show the

shape of the molecule. Nevertheless, the systematic classification and study of organic compounds is based on the use of these formulas for the representation of structural relationships.

The Methane Series of Hydrocarbons. The simplest of the hydrocarbons is methane, also known as marsh gas, because it is formed by the anaerobic fermentation of vegetable matter beneath the surface of water in marshes. The series of hydrocarbons of which methane is the simplest member is known as the methane series. These substances have little chemical activity and are also known as *paraffin hydrocarbons*. The methane series is an homologous series, in which the constant difference between successive members is CH_2, and the entire series may be represented by the type formula C_nH_{2n+2}, in which n is the number of atoms of carbon in a molecule. A few of the lower members of the series are: methane, CH_4, ethane, C_2H_6, propane, C_3H_8, butane, C_4H_{10}. The names of the hydrocarbons of the methane series after the first four are derived from the Greek numeral for the number of carbon atoms in one molecule of each compound, and all of the names end with the suffix *-ane*. The structural formulas for the first three members of the series are written in the preceding paragraph. The common difference, CH_2, between any member and its next higher homologue is due to the replacement of an atom of hydrogen by a —CH_3 group. The structural relationships in organic compounds are frequently indicated by condensed formulas, *e.g.*, methane, CH_4, ethane, CH_3CH_3, and propane, $CH_3CH_2CH_3$.

No isomers of the first three members of the series are known, but there are two compounds with the composition shown by the molecular formula C_4H_{10}. Only one arrangement of the atoms is possible in each of the first three members according to the principles of structural formulas, but two different arrangements may be made for butane. The methyl group, —CH_3, may be substituted for an atom of hydrogen on one of the terminal carbon atoms or on the intermediate carbon in propane. In the first instance, the structure shows the atoms in a straight chain, while the second gives a branched chain. The straight chain hydrocarbon, having the molecular formula C_4H_{10}, is normal butane, *n*-butane, and the other isobutane. The structural relationships of these two isomers are shown by the formulas:

$$
\begin{array}{ccccc}
 & \text{H} & \text{H} & \text{H} & \text{H} \\
 & | & | & | & | \\
\text{H} - & \text{C} - & \text{C} - & \text{C} - & \text{C} - \text{H} \\
 & | & | & | & | \\
 & \text{H} & \text{H} & \text{H} & \text{H}
\end{array}
\qquad
\begin{array}{cccc}
 & \text{H} & \text{CH}_3 & \text{H} \\
 & | & | & | \\
\text{H} - & \text{C} - & \text{C} - & \text{C} - \text{H} \\
 & | & | & | \\
 & \text{H} & \text{H} & \text{H}
\end{array}
$$
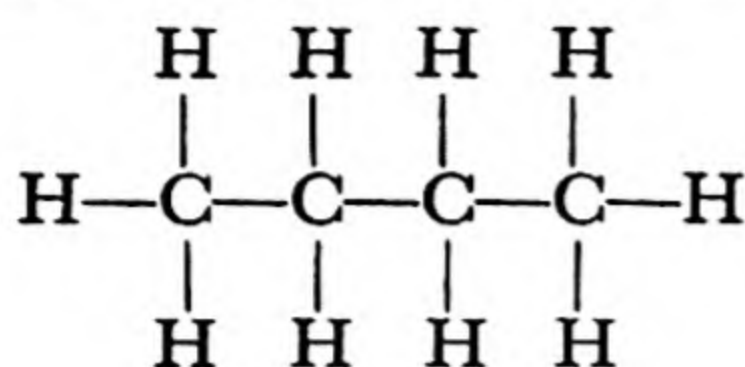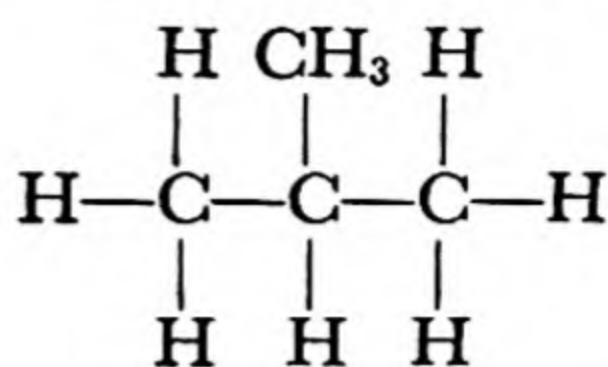
<div align="center">
Butane   Isobutane
</div>

There are three structural isomers having the molecular formula C_5H_{12}, and the number of geometrical patterns increases rapidly with the number of carbon atoms in the molecule.

Properties of the Hydrocarbons of the Methane Series. The melting points and boiling points of some of the normal or straight chain hydrocarbons of the methane series are shown in Table 46. The compounds are listed in the order of increasing complexity and, consequently, increasing molecular weight. After the first few members, a rise in the melting and boiling points is observed with increasing molecular weight.

TABLE 46. NORMAL HYDROCARBONS OF THE METHANE SERIES

Name	Formula	Melting Point (° C.)	Boiling Point (° C.)
Methane	CH_4	− 182	− 161
Ethane	C_2H_6	− 183	− 88
Propane	C_3H_8	− 187	− 42
Butane	C_4H_{10}	− 139	1
Pentane	C_5H_{12}	− 135	36
Hexane	C_6H_{14}	− 95	69
Heptane	C_7H_{16}	− 91	98
Octane	C_8H_{18}	− 57	126
Nonane	C_9H_{20}	− 54	151
Decane	$C_{10}H_{22}$	− 30	174
—		—	—
Hexadecane	$C_{16}H_{34}$	20	287

In general, the freezing points and boiling points of the isocompounds are lower than those of the normal substances. The melting and boiling points of isobutane, for example, are − 145° and − 10°, respectively.

Reactions of the Hydrocarbons of the Methane Series. These substances may be ignited by heating them in air or oxygen, and they burn with the formation of water and carbon dioxide. The higher members of the series are less active than the lower members. Some of the lower members of the series react with chlorine and

with bromine in direct sunlight, forming products containing halogens in place of the hydrogen of the hydrocarbon.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
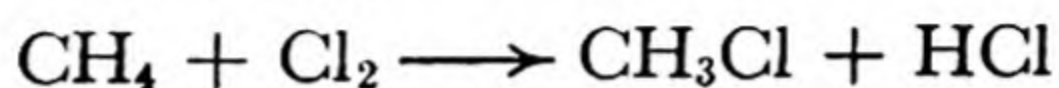
The reaction is known as a substitution reaction. Hydrocarbons that may react with other substances only through substitution are known as saturated hydrocarbons. Substitution may take place in several stages, producing a mixture of products.

Preparation of the Hydrocarbons of the Methane Series. Industrial products containing mixtures of these hydrocarbons are obtained by the fractionation of petroleum and by the destructive distillation of coal. The pure hydrocarbon may be prepared by the action of water on the Grignard reagent, produced by the reaction of magnesium with the halogen derivative of the hydrocarbon. For example, in dry ether, ethyl bromide reacts with magnesium to form ethyl magnesium bromide, which may be decomposed by water to produce pure ethane.

$$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$$
$$C_2H_5MgBr + H_2O \longrightarrow C_2H_6 + Mg(OH)Br$$
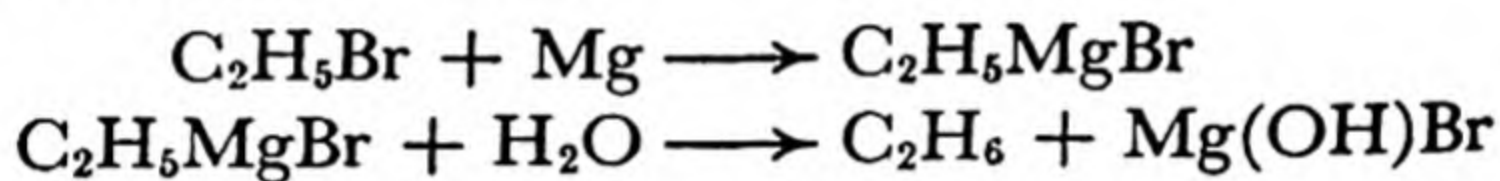
Higher members of the series may be prepared by the reaction of metallic sodium with the halogen derivatives, which contain the desired organic groups to produce the hydrocarbon. The reaction is known as the Wurtz reaction. Propane may be prepared in this manner from a mixture of methyl and ethyl iodides.

$$CH_3I + C_2H_5I + 2\,Na \longrightarrow CH_3CH_2CH_3 + 2\,NaI$$
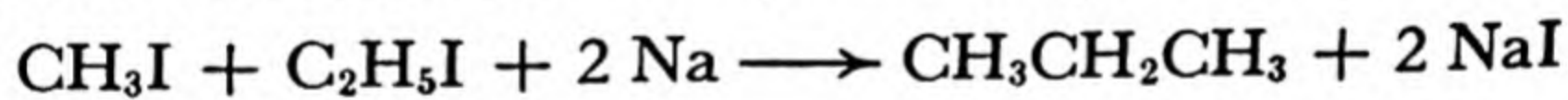
Usually, a mixture of products is obtained in this reaction, and therefore it is necessary to separate these substances. This separation may offer difficulties if the boiling points of the products are close together.

The Olefins. Unsaturated Hydrocarbons. *Ethylene,* **C₂H₄,** is the first member of a series of hydrocarbons in which each member contains a smaller percentage of hydrogen than the corresponding member of the methane series. This series is represented by the type formula **C$_n$H$_{2n}$.** The names of the olefins are derived from the names of the corresponding paraffins by using the suffix *-ylene* in place of *-ane,* but they are more commonly named through the use of the suffix *-ene.* The hydrocarbons of the ethylene series are

known as unsaturated hydrocarbons, because their molecules contain an insufficient number of hydrogen atoms to form covalent bonds with all of the available electrons in the carbon atoms. This results in the sharing of two electron pairs between two of the carbon atoms, forming a double bond as shown in the electronic and structural formulas for ethylene.

$$H : \overset{\cdot\cdot}{C} :: \overset{\cdot\cdot}{C} : H \qquad H - \overset{\overset{\displaystyle H}{|}}{C} = \overset{\overset{\displaystyle H}{|}}{C} - H$$

The successive homologues in this series bear the same relation to each other as those in the methane series. There are two isomeric butenes that differ in the location of the double bond. A number preceding the name of the unsaturated hydrocarbon indicates the position of the double bond. Thus, the double bond is attached to a terminal carbon in 1-butene and to a carbon atom next to the end of the chain in 2-butene.

Propene   1-Butene   2-Butene
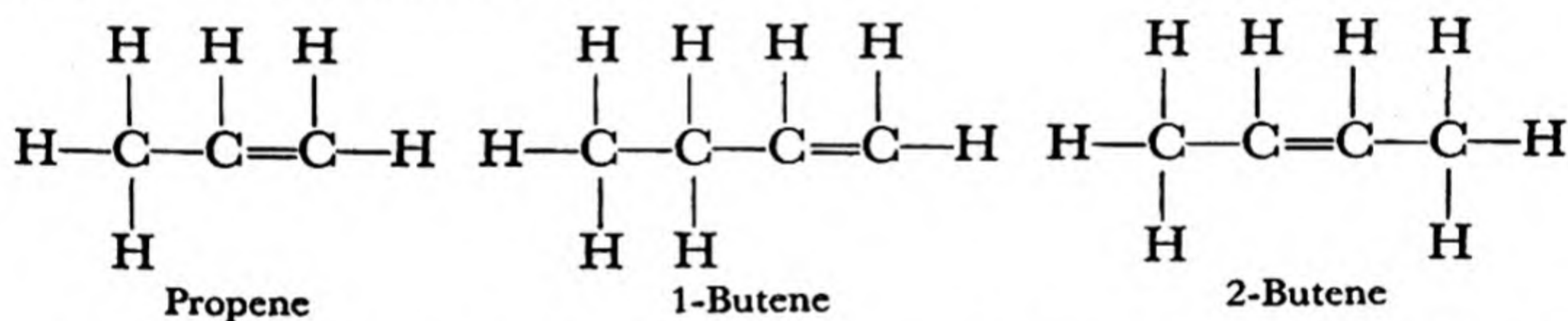
The unsaturated hydrocarbons may undergo addition reactions with hydrogen, with the halogens, and with a number of other substances, forming saturated products. The color of free bromine disappears, and ethylene bromide, $C_2H_4Br_2$, is formed when ethylene is passed into a solution of bromine.

$$H - \overset{\overset{\displaystyle H}{|}}{C} = \overset{\overset{\displaystyle H}{|}}{C} - H + Br_2 \longrightarrow H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - H$$
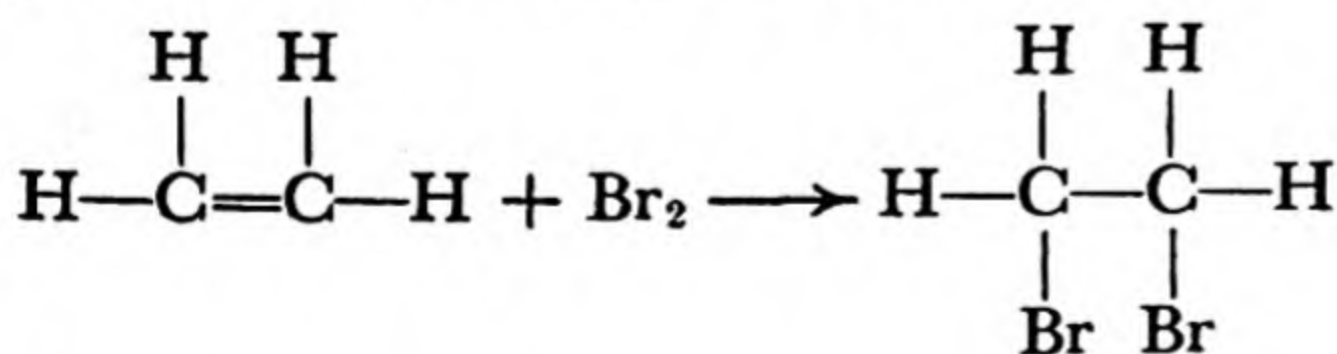
In contact with a catalyst propene adds hydrogen to form propane.

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{C} = \overset{\overset{\displaystyle H}{|}}{C} - H + H_2 \longrightarrow H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - H$$
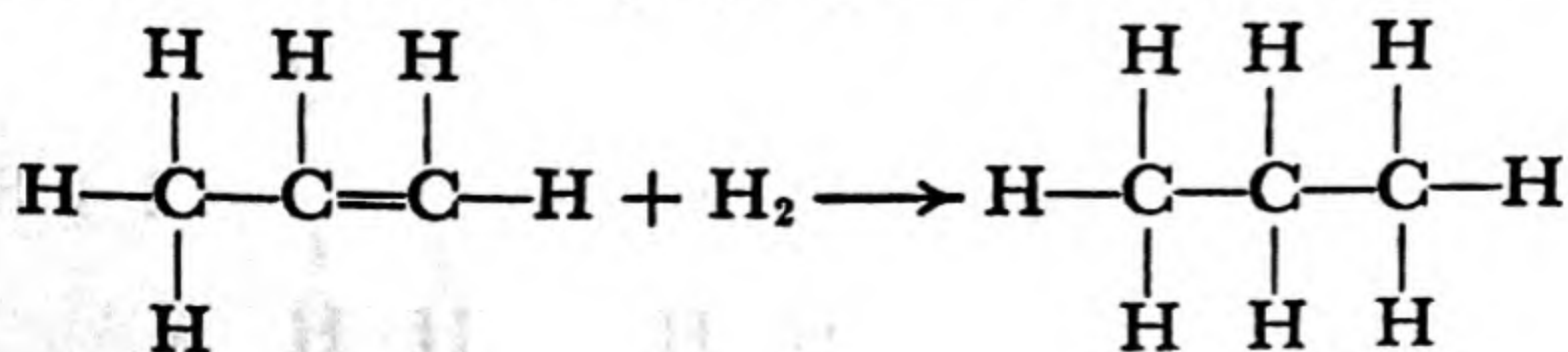
Olefins are usually prepared in laboratory practice by dehydrating alcohols with concentrated sulfuric acid. Thus, ethylene is prepared by the dehydration of ethanol at 180°.

$$\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{H—C}}}—\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}—\text{OH} + H_2SO_4 \longrightarrow H—\overset{\overset{\text{H}}{|}}{\text{C}}=\overset{\overset{\text{H}}{|}}{\text{C}}—H + H_2SO_4(H_2O)$$
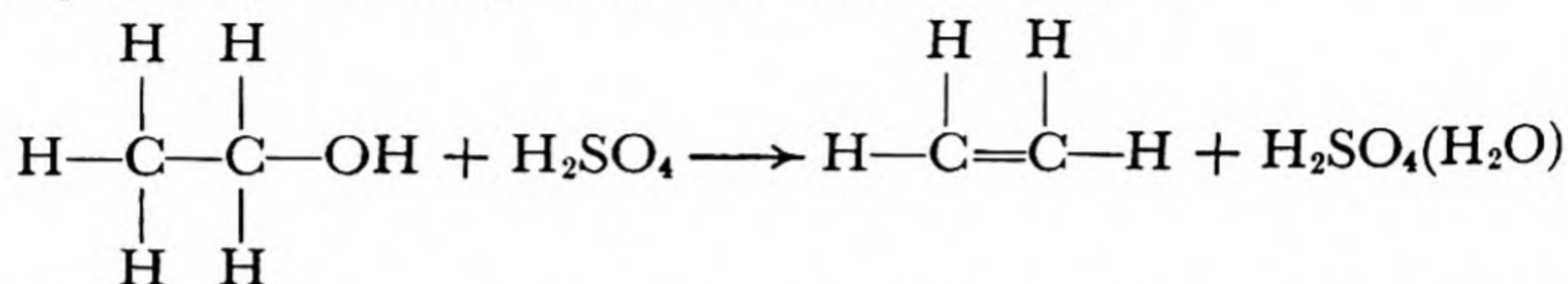
Ethylene may be prepared industrially by the catalytic dehydration of ethanol over hot aluminum oxide. Large quantities of olefins are also produced as products of the thermal decomposition of paraffin hydrocarbons of high molecular weight, as in petroleum cracking. (See page 565.)

Ethylene is used as an anaesthetic in surgery. It is also used to hasten the ripening of fruit, such as bananas and the citrus fruits, usually picked green for transportation. Ethylene is used widely in chemical industry for the production of a number of important compounds. Ethylene and hydrogen chloride react in the presence of antimony chloride as a catalyst to form ethyl chloride, used in the production of tetraethyl lead.

$$H—\overset{\overset{\text{H}}{|}}{\text{C}}=\overset{\overset{\text{H}}{|}}{\text{C}}—H + HCl \longrightarrow H—\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}—\underset{\underset{\text{Cl}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}—H$$
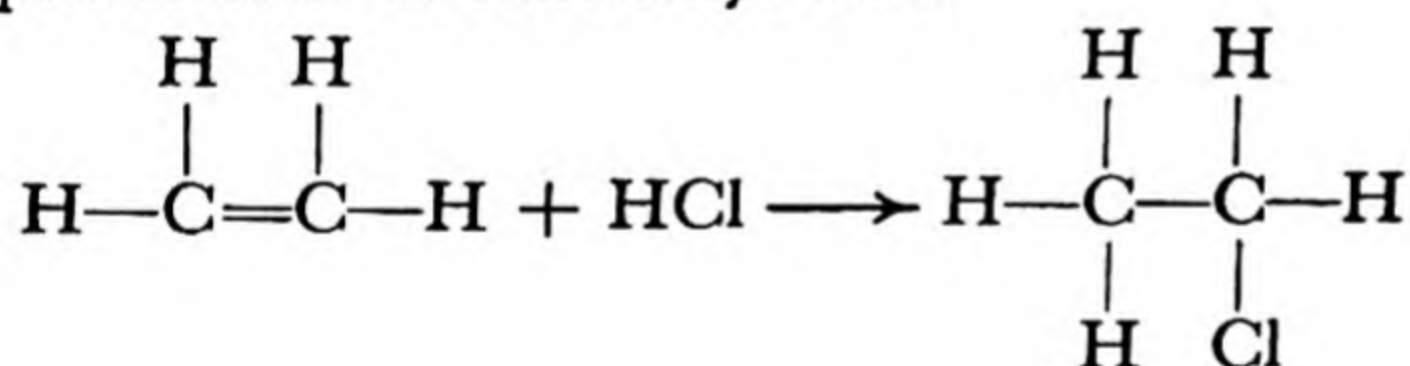
Ethylene dibromide is used with tetraethyl lead in ethyl gasoline. Hypochlorous acid combines with ethylene to form ethylene chlorhydrin, used in the production of ethylene glycol for an antifreeze in automobile radiators and a cooling liquid for airplane engines. Ethylene reacts with benzene to form ethyl benzene, which is then oxidized and dehydrated to form the unsaturated product, styrene, $C_6H_5CH=CH_2$, used in the production of *Buna S* rubber. The reaction of ethylene with sulfur monochloride produces dichlorodiethyl sulfide, mustard gas, a chemical warfare agent.

$$2\,H—\overset{\overset{\text{H}}{|}}{\text{C}}=\overset{\overset{\text{H}}{|}}{\text{C}}—H + S_2Cl_2 \longrightarrow Cl—\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}—\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}—S—\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}—\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}—Cl + S$$
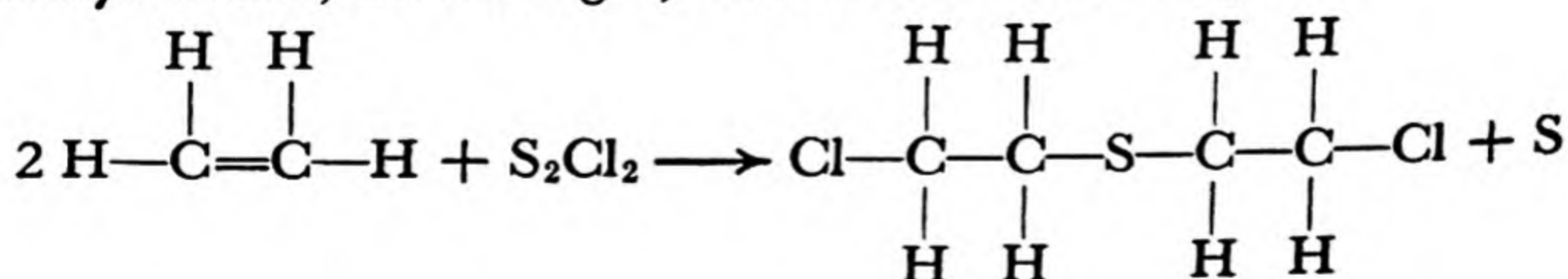
The Acetylenes. The members of this series contain still smaller percentages of hydrogen than the corresponding olefins. The type formula for the series is C_nH_{2n-2}. The simplest hydrocarbon of this series is acetylene, C_2H_2. One hydrogen atom is attached to each carbon atom in the molecule, and the six remaining electrons constitute a triple bond, $H—C{\equiv}C—H$. Acetylene is prepared by the reaction of water with calcium carbide.

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
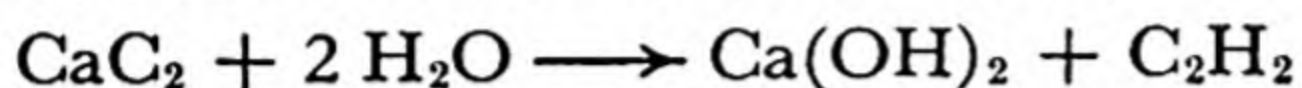
It is also produced by thermal decomposition in the cracking of petroleum hydrocarbons at high temperatures. Acetylene is an endothermic compound with a high heat of combustion. Its familiar use in the oxyacetylene blowpipe is an application of this property.

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 624{,}000 \text{ cal.}$$
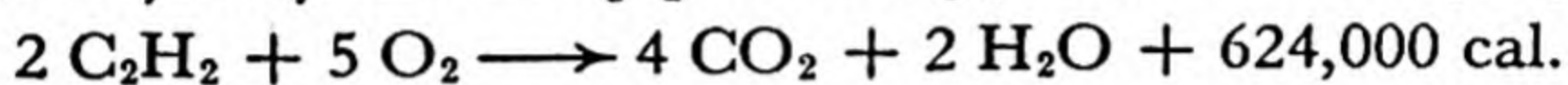
Acetylene is an unsaturated compound, which may add successively two molecules of hydrogen or of the halogens.

$$H—C{\equiv}C—H + H_2 \longrightarrow H—\overset{\displaystyle H}{\underset{}{C}}{=}\overset{\displaystyle H}{\underset{}{C}}—H$$

$$H—\overset{\displaystyle H}{\underset{}{C}}{=}\overset{\displaystyle H}{\underset{}{C}}—H + H_2 \longrightarrow H—\overset{\displaystyle H}{\underset{\displaystyle H}{C}}—\overset{\displaystyle H}{\underset{\displaystyle H}{C}}—H$$
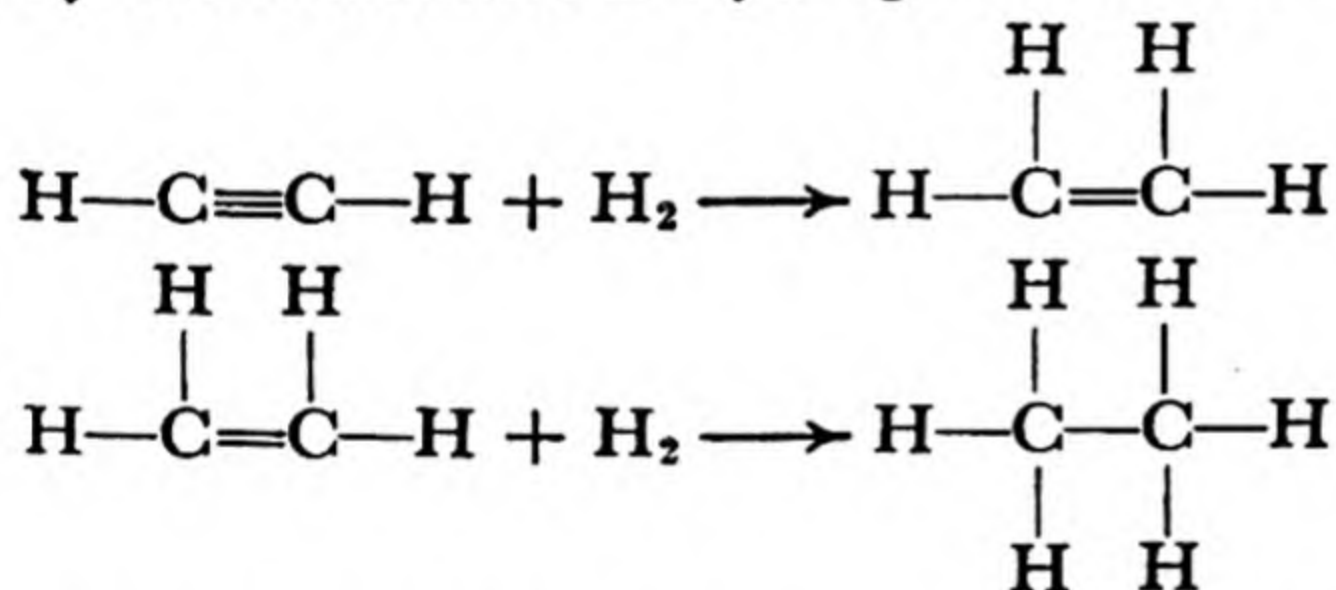
The saturated product, formed by the reaction of acetylene with bromine, is tetrabromoethane.

$$H—C{\equiv}C—H + 2\,Br_2 \longrightarrow H—\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}—\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}—H$$
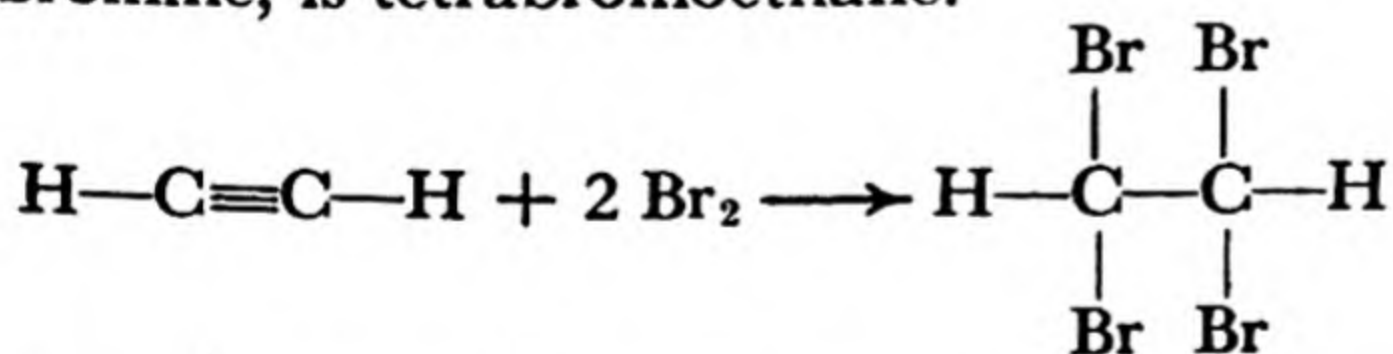
Water and acetylene undergo an addition reaction in the presence of an acidic mercuric sulfate solution as a catalyst to form an unstable hydroxy compound known as vinyl alcohol, which undergoes rearrangement to form acetaldehyde. (See page 576.)

$$H—C{\equiv}C—H + H_2O \longrightarrow \left[H—\overset{\displaystyle H}{\underset{}{C}}{=}\overset{\displaystyle OH}{\underset{}{C}}—H \right] \longrightarrow H—\overset{\displaystyle H}{\underset{\displaystyle H}{C}}—\overset{\displaystyle O}{\underset{}{C}}—H$$
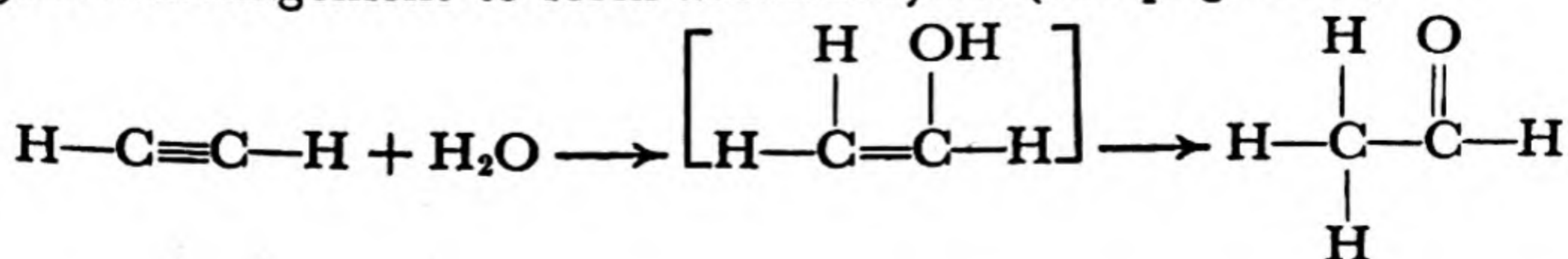
Acetic acid and a number of other important products may be prepared from acetaldehyde.

These unsaturated hydrocarbons undergo polymerization readily, adding molecule to molecule to form more complex products. Thus, acetylene in the presence of cuprous salts as catalyst yields vinyl acetylene.

$$2 \; H-C\equiv C-H \longrightarrow H-C\equiv C-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H$$
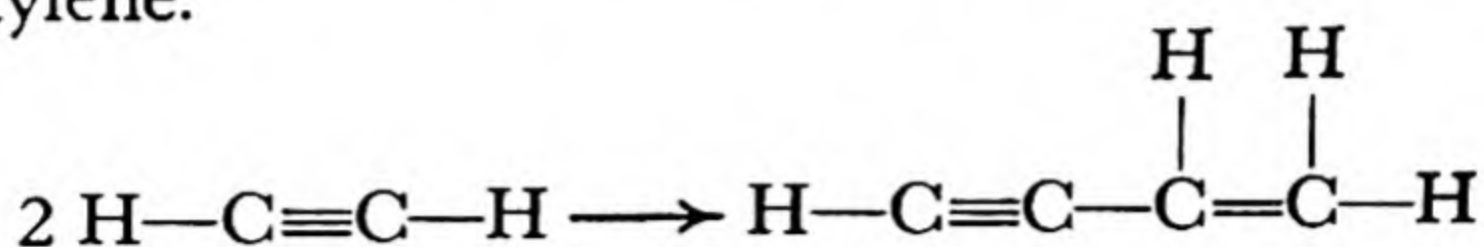
This is the first step in the production of the synthetic rubber, *neoprene*, from acetylene.

Diolefins. Dienes. The molecules of the dienes have two points of unsaturation. The members of this series are isomeric with the corresponding acetylenes, and the type formula is C_nH_{2n-2}. The simplest member of the series is allene, $CH_2=C=CH_2$. The most important of the dienes are butadiene and isoprene. The structural similarity of these compounds is shown by the formulas.

$$H-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H \qquad\qquad H-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle CH_3}{|}}{C}-\!\!-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H$$

1-,3-Butadiene Isoprene
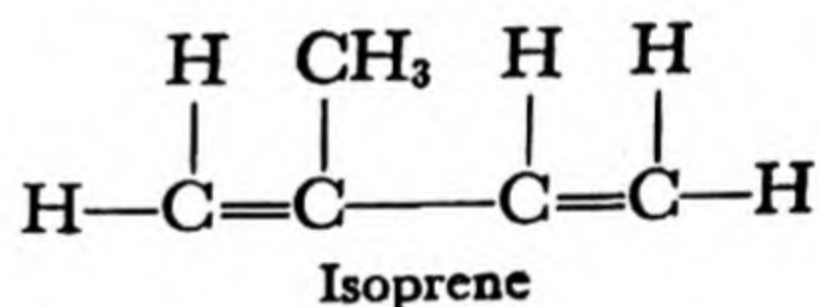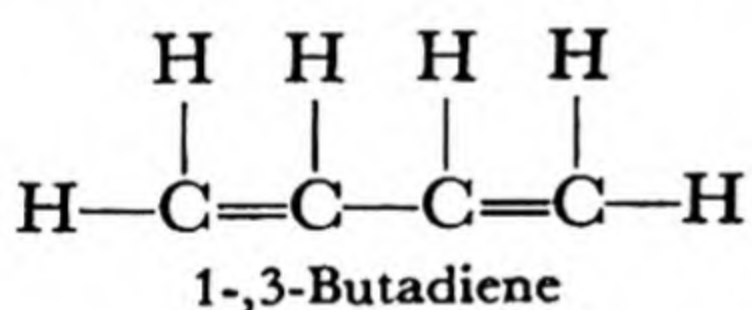
Isoprene is formed when rubber, *caoutchouc*, is heated in the absence of air, and the analysis of rubber shows it to be a polymer of isoprene, $(C_5H_8)_n$. The number of isoprene units is estimated to be about a thousand. The dienes undergo the addition reactions exhibited by the other unsaturated hydrocarbons. They also polymerize readily to form long chainlike molecules, which exhibit many of the properties of rubber. The most extensive production of synthetic rubber is based on the polymerization of butadiene.

There are two important sources of butadiene, petroleum hydrocarbons and ethanol, ethyl alcohol. Butadiene is produced from n-butane by dehydrogenation in contact with suitable catalysts, i.e., by the removal of hydrogen atoms from the molecules of n-butane without replacement. Normal butane is obtained in large quantities from petroleum.

$$CH_3CH_2CH_2CH_3 \longrightarrow H_2 + CH_3CH_2CH=CH_2$$
$$CH_3CH_2CH=CH_2 \longrightarrow H_2 + CH_2=CHCH=CH_2$$
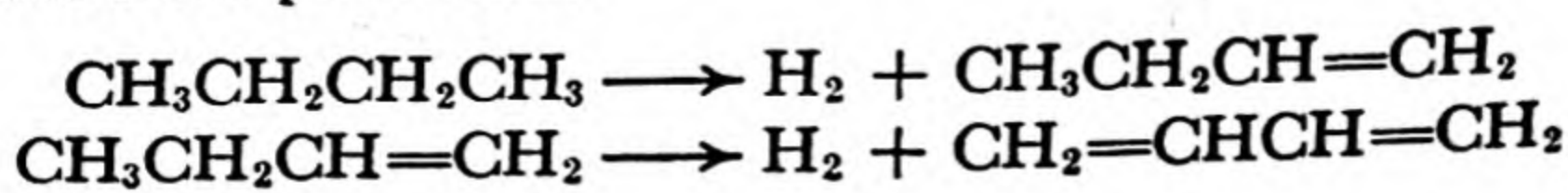
Butenes, which are produced during the cracking of the petroleum hydrocarbons, may be converted directly into butadiene.

Butadiene is produced by the dehydrogenation and dehydration of ethanol at temperatures of 400–425° in contact with catalysts such as aluminum oxide and zinc oxide. The mechanism of the reactions is complex, and the processes usually require more than one stage. The essential changes may be represented by the following equations:

$$C_2H_5OH \longrightarrow CH_3CHO + H_2$$
$$C_2H_5OH + CH_3CHO \longrightarrow CH_2{=}CHCH{=}CH_2 + 2\,H_2O$$

Synthetic Rubber. The production of rubber by the polymerization of isoprene has not been carried out successfully, but the production of rubberlike products, *elastomers*, from butadiene and other similar molecules has proved successful. The polymerization of butadiene produces Buna rubber. The quality of the Buna rubbers has been greatly improved by condensing butadiene with other unsaturated compounds to produce *copolymers*. *Buna S*, the copolymer of butadiene and styrene, is produced in colloidal suspension by the emulsification of the materials in water before adding the proper polymerizing agent. This product is superior to natural rubber in resistance to heat and to abrasion, and is used in the manufacture of tires.

Neoprene, a second important synthetic rubber is produced from acetylene. Vinyl acetylene undergoes an addition reaction with hydrogen chloride in the presence of cuprous salts to form chloroprene.

$$\underset{\displaystyle H-C{\equiv}C-\overset{\displaystyle H}{\underset{|}{C}}{=}\overset{\displaystyle H}{\underset{|}{C}}-H + HCl \longrightarrow H-\overset{\displaystyle H}{\underset{|}{C}}{=}\overset{\displaystyle Cl}{\underset{|}{C}}-\overset{\displaystyle H}{\underset{|}{C}}{=}\overset{\displaystyle H}{\underset{|}{C}}-H}{}$$
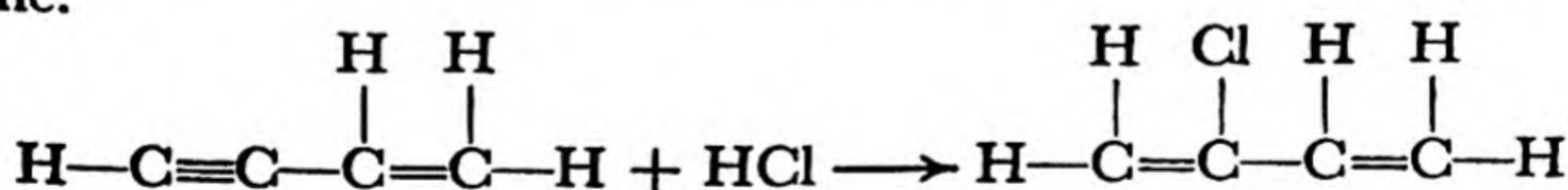
This compound resembles isoprene and butadiene in structure and readily undergoes polymerization to form a rubberlike product. Neoprene does not possess good abrasion resistance and is not used for the manufacture of tires, but it is extensively used in gasoline and oil lines for which rubber is not suited.

Butyl rubber is a copolymer of butadiene and isobutylene. It is not attacked by oxygen and a number of other chemical agents. *Thiokol* resins are produced by the reaction of chlorinated olefins,

chiefly ethylene dichloride, with solutions of sodium tetrasulfide, Na_2S_4. A rubberlike product is obtained with an excess of the sulfide. Its chief use is in making flexible tubes and linings for tanks in the oil industry, because it is not affected by the hydrocarbons.

Aromatic Hydrocarbons. The hydrocarbons of the series discussed in the preceding paragraphs are characterized by an open chain structure. Such compounds are known as *aliphatic hydrocarbons*. A number of hydrocarbons, structurally different from these substances, are produced by the destructive distillation of coal. These substances are known as *aromatic hydrocarbons*. They may be separated from coal tar, a complex material condensed from the gaseous products distilled from coal. The simplest series of aromatic hydrocarbons is the *benzene series*, which is represented by the type formula, C_nH_{2n-6}. The small percentage of hydrogen in these substances and their ability to undergo addition reactions indicate that they are unsaturated compounds. Nevertheless, addition reactions are not pronounced in their behavior, and they undergo substitution reactions much more readily. In their reactions with the halogens, the hydrocarbons of the benzene series resemble the paraffins more closely than the olefins.

Benzene, C_6H_6, is the first member of the benzene series. The reactions of benzene and its homologues show that the molecules contain a group of six carbon atoms, held together by such strong forces that they are not decomposed by the action of a number of chemical agents. Each of the hydrogen atoms in the benzene molecule is chemically equivalent to each of the others, indicating a symmetrical structure with one hydrogen atom attached to each carbon atom. In 1865, Kekulé suggested the structural formula of carbon atoms arranged in a hexagon, forming a closed ring structure, known as the *benzene ring*. Alternate double bonds indicate unsaturation, in accord with the fact that these compounds may add six monovalent atoms per molecule. The hydrogenation of benzene produces the saturated product cyclohexane, C_6H_{12}, instead of hexane, C_6H_{14}, the saturated open-chain hydrocarbon containing six atoms of carbon per molecule. The second member of the series, toluene, has the molecular formula C_7H_8. The structural formulas of these substances are:
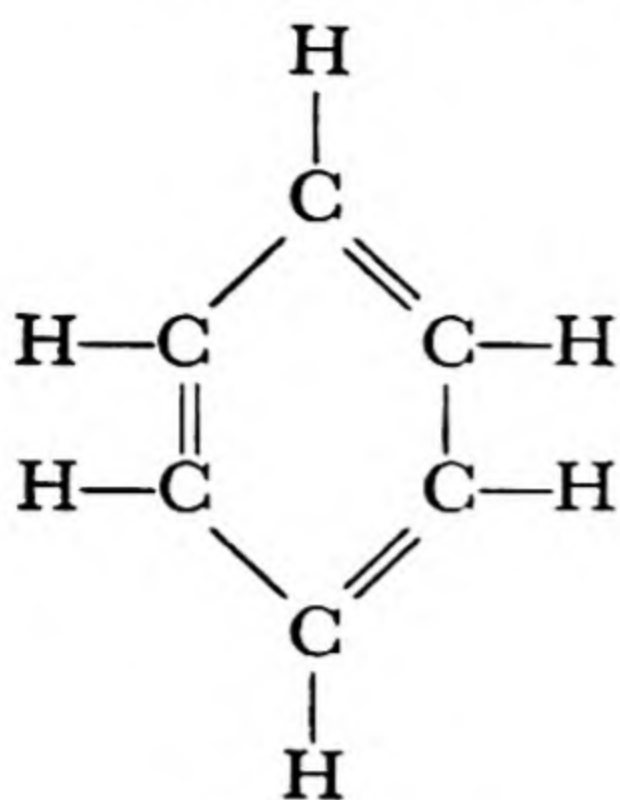
Benzene
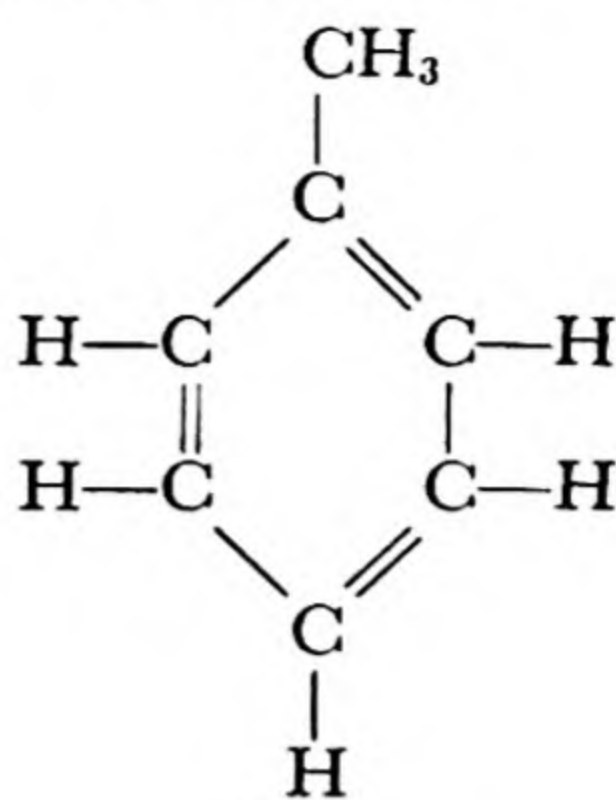
Toluene

For practical purposes an outline formula is commonly used, in which the benzene ring is represented by a hexagon. The symbols of the carbon atoms and of the hydrogen atoms directly attached to the carbon atoms in this nucleus of the molecule are omitted, but any substituent groups or atoms in homologues or derivatives are written. The following formulas illustrate this practice.

Benzene
C_6H_6

Toluene
$C_6H_5CH_3$

Bromobenzene
C_6H_5Br
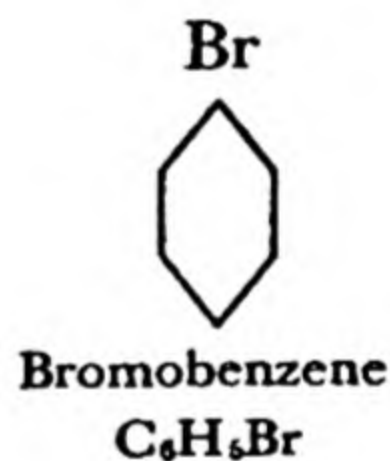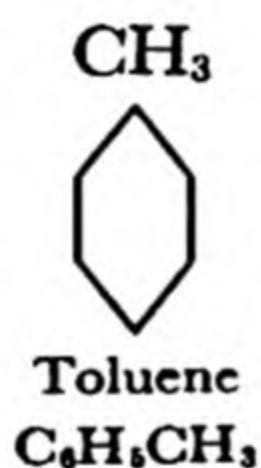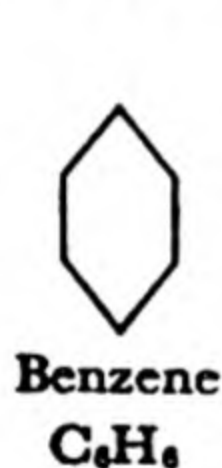
There are three isomers with the composition shown by the condensed formula $C_6H_4(CH_3)_2$. These substances are *xylenes*. There is also a fourth isomer, *ethyl benzene*, in which the additional methyl group is substituted for an atom of hydrogen in the methyl group already present in toluene, instead of an hydrogen atom attached to one of the carbon atoms in the ring structure. Consideration of the structure and the properties of the xylenes reveals the significance of the position of the substituting groups. One methyl group being already attached to a carbon atom in the benzene ring, there are three positions relative to this into which a second group may enter. These positions, known as ortho-, para-, and meta-, are shown in the following formulas for the three xylenes.

CH₃ (structures)
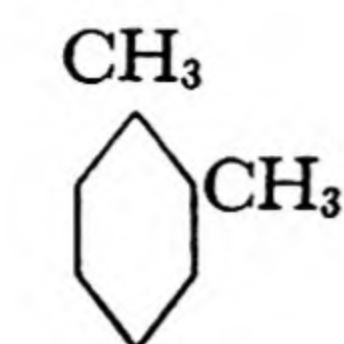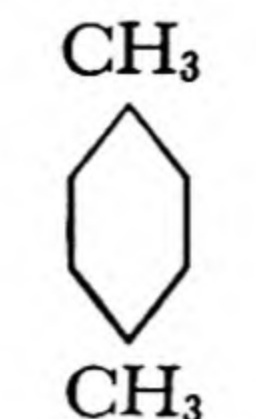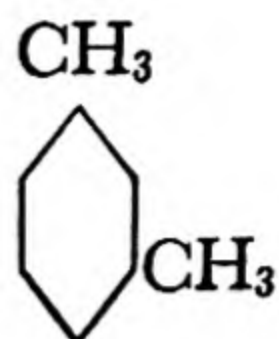
o-Xylene   p-Xylene   m-Xylene

Reactions of benzene with the halogens, with nitric acid, and with sulfuric acid are considered in the following chapter in connection with the formation of some derivatives.

Benzene and toluene are normally produced in sufficient quantities for industrial use by the destructive distillation of coal. However, the demand for the production of explosives is so great in times of war that other sources are needed. During World War I, the only important source of toluene was as a by-product of coke. This led to a great expansion of by-product coke ovens, in preference to beehive ovens, in the steel industry. Methods are now available for the production of toluene from n-heptane, itself obtained from petroleum. The process requires the action of catalysts, which lead to the removal of hydrogen and the formation of the benzene ring, leaving the seventh carbon together with its three atoms of hydrogen as the methyl group of toluene.

Coal. The decomposition of vegetable matter in the absence of air, as beneath the surface of water in a swamp, leads to the formation of peat. Further decomposition of the peat, with the loss of volatile matter, produces lignite or brown coal. If a mass of this material is subjected to high temperature and great pressure, as has happened in past geologic ages in great land upheavals, the transformation proceeds further, the organic compounds partially decompose with the formation of volatile materials, and first bituminous and then anthracite coal are produced. The composition of coal varies greatly from one deposit to another, but it is made up largely of amorphous carbon and contains also complex compounds of carbon and hydrogen.

Destructive Distillation of Coal. The decomposition of the carbon compounds remaining in coal takes place at about 1000°, leaving a residue composed of carbon and mineral matter such as silicates. A number of volatile products are formed by the decomposition of coal. These materials, known as by-products of coke,

are so important that most of the coke used in the metal industries in the United States is now produced in by-product coke ovens.

The hot gas mixture from the ovens is passed through condensers and scrubbers, where water, coal tar, and ammonia are removed. A portion of the benzene and toluene condenses in the coal tar, but a portion is carried along by the gas and may be removed by absorption in a heavy oil in one of the scrubbers. The gas is then passed over trays, containing iron oxide, in the purifiers where sulfides and cyanides are removed. *Coal gas* contains approximately 50 per cent of hydrogen, 35 per cent of methane, 8 per cent of carbon monoxide, and 2 per cent of other hydrocarbons, the remainder being chiefly nitrogen. This gas has high fuel value.

Coal tar is a black, viscous liquid containing a number of hydrocarbons and other substances important in the production of dyes, drugs, explosives, plastics, and other materials. Coal tar may be separated into several fractions by distillation. Further refining yields the following products: a light oil from which benzene, toluene, and the xylenes may be separated; a middle oil containing phenol, the cresols, and naphthalene; a heavy oil containing cresols and phenol; a green oil containing anthracene; and a complex pitch which still contains the bulk of the matter in the tar. If the destructive distillation of coal is carried out at 500–600°, the low temperature carbonization of coal, a tar is obtained from which liquid fuels may be produced, similar to the fractions from petroleum.

Natural Gas. In some localities, gaseous products formed during the conversion of organic matter into coal and oil have been trapped beneath impervious layers. This material, known as natural gas, is found in several states in the United States. It consists chiefly of hydrocarbons, 80–95 per cent methane. The heat of combustion of methane is large.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 213,500 \text{ cal.}$$
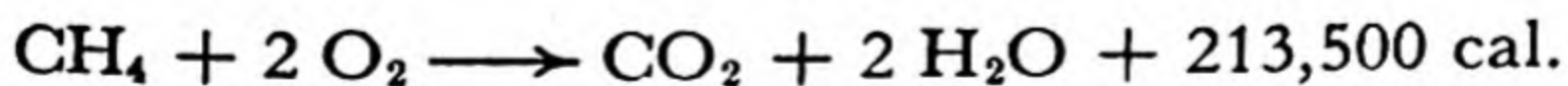
Consequently, this gas has high value as a fuel. It is now secured in great quantities from natural accumulations and distributed by means of pipe lines to industrial centers.

Petroleum. Liquid products of the decomposition of organic matter have accumulated at varying depths beneath the surface in

many locations on the earth. This material is a dark-colored, viscous liquid known as petroleum, "rock oil." It is a complex liquid mixture used as the source of a great number and variety of industrial products.

The composition of petroleum varies greatly by localities, but the principal components are saturated hydrocarbons. Both paraffin hydrocarbons and other saturated hydrocarbons with ring structure occur in petroleum. The various substances in petroleum have
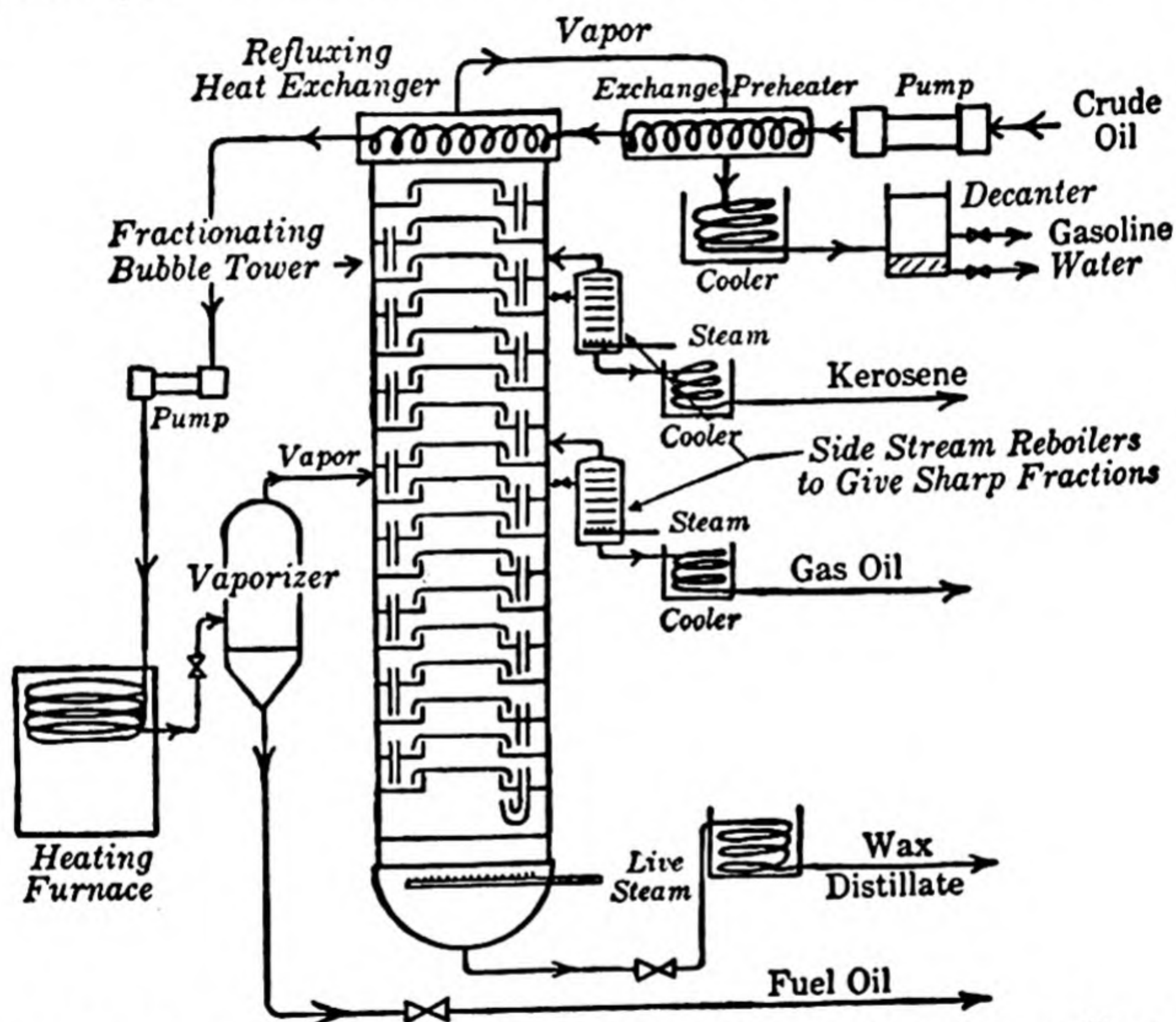
Fig. 134. Diagram of a Modern Crude Oil Distillation Unit (From Conant, The Chemistry of Organic Compounds)

different boiling points, and the more volatile components may be separated from the less volatile by *fractional distillation*. In the modern distillation unit (Fig. 134), the vapors are passed into a "bubble tower," divided into a number of sections. The substances with higher boiling points condense in the lower sections and flow down through the tower from plate to plate. The hot gases from the furnace bubble through these liquid products and the gasoline fraction passes out at the top of the column and is condensed sepa-

rately. Other fractions are withdrawn at different levels. These commercial products are not specific single substances. Consequently, the temperature limits for the collection of the various fractions may be set arbitrarily. Kerosene is condensed in the upper part of the column, gas oil at the middle height, and fuel oils, the product with high boiling point, in the lower portion. Fuel oil is redistilled with steam and separated into light, medium, and heavy oils. Vaseline and paraffin may be separated from the higher boiling fraction. A tar residue remains after the distillation of the oil fractions. This is used in the manufacture of roofing and as an artificial asphalt in pavements.

A variety of products may be separated from petroleum, and still others may be secured by synthetic processes using these substances as crudes. The most important of the petroleum products are motor fuels, fuel oils, and lubricating oils. An approximate distribution of the refined products obtained by the distillation of petroleum is shown in Table 47.

TABLE 47. PRODUCTS FROM PETROLEUM

Product	Temperature (°C.)	Composition	Use
Gas	Up to 30	CH_4–C_4H_{10}	Fuel
Petroleum ether	30–100	C_5H_{12}–C_7H_{16}	Solvent
Gasoline	70–200	C_6H_{14}–$C_{12}H_{26}$	Motor fuel
Kerosene	200–275	$C_{12}H_{26}$–$C_{16}H_{32}$	Illuminant, Fuel
Gas oil	Above 275	$C_{16}H_{32}$–$C_{18}H_{33}$	Fuel oil, Cracking stock
Lubricating oil	—	$C_{16}H_{34}$–$C_{20}H_{42}$	Lubricant
Greases, vaseline	—	$C_{18}H_{38}$–$C_{22}H_{46}$	Lubricant
Paraffin	—	$C_{20}H_{42}$–$C_{24}H_{50}$	Candles, etc.
Tar (asphalt)	—	—	Roofing, Pavement

Natural gas, which occurs in many of the petroleum fields, contains small percentages of volatile hydrocarbons with boiling points above ordinary temperatures. These substances may be condensed from the gas under high pressures and may be absorbed by charcoal. This product is known as *casing-head gasoline*. It is a volatile liquid that may be mixed with higher boiling fractions, obtained during the straight distillation of petroleum, to make a blended gasoline.

A cracking process for the thermal decomposition of hydrocarbons of high boiling point, to form substances of lower boiling points

in the gasoline range, was discovered by Burton in 1913. Although a large number of products may be produced, the decomposition may be illustrated by the following equations.

$$C_{16}H_{34} \longrightarrow C_8H_{18} + C_7H_{16} + C$$
$$C_{16}H_{34} \longrightarrow C_8H_{18} + C_8H_{16}$$
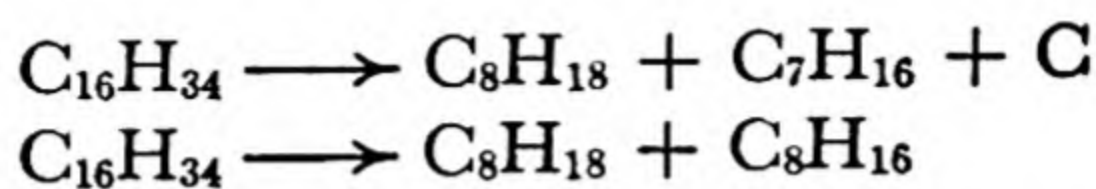
Thus, saturated and unsaturated hydrocarbons and free carbon are produced during the cracking process. Large quantities of gaseous hydrocarbons, such as methane, ethylene, butane and others, are formed, since the molecular split does not necessarily occur between any two specific atoms of carbon. The importance of some of these substances has been mentioned. Cracking may take place in the liquid phase at pressures of 100–1000 lb. per square inch and at temperatures of 400–500°. In other processes, cracking occurs in the gas phase and at temperatures up to 600°. Catalysts are employed in many of the processes. In the McAfee process, for example, anhydrous aluminum chloride serves as a catalyst. In some of the processes, *hydrogenation* accompanies cracking. The oil is heated with hydrogen at high pressure in contact with the catalyst. In this manner the yield is further increased.

The hydrogenation of coal to produce liquid fuels was developed in Germany by Bergius. The pulverized coal is suspended in a suitable liquid vehicle and heated to a temperature of 400–500°, with hydrogen under a pressure of about 250 atmospheres. The liquid product may be fractionated, cracked, and further hydrogenated for the preparation of gasoline, fuel oils, and lubricating oils, as in the treatment of petroleum.

The polymerization of certain gaseous hydrocarbons to form liquid products further augments the supply of liquid fuels. Gaseous hydrocarbons of low molecular weight, formed in the cracking process, may be polymerized at 500–600° and at pressures of 1000–3000 lb. per square inch. Catalytic processes at lower temperatures and pressures are also used. Hydrocarbons of the paraffin type may be converted into olefins for use in the polymerization processes.

Since the composition of gasoline from different sources varies, the properties vary also. Many of the gasolines "knock" badly in high compression engines, because of the detonation of the

gas-air mixture. The paraffin hydrocarbons in general are worse than the aromatic and olefinic hydrocarbons. The rating of a gasoline in its antiknock properties is determined by using it in a special engine having high compression. The knocking is recorded electrically by means of a bouncing pin, which makes an electrical contact each time the engine knocks. The antiknock rating is expressed in terms of *octane number*. The octane number is the percentage of iso-octane in a mixture with normal heptane giving the same antiknock characteristics as the gasoline under examination. The antiknock properties of gasoline may be improved by blending products from different sources. Tetraethyl lead is now used in most gasoline as a negative catalyst, decreasing the rate of reaction of the gasoline-air mixture sufficiently to prevent detonation. Ethylene dibromide is added along with tetraethyl lead in the preparation of *ethyl gasoline*, to form lead bromide during the combustion of the gasoline in internal combustion engines, instead of lead oxide. The bromide escapes in the exhaust gases, while lead oxide melts and corrodes the spark points.

EXERCISES

1. What is the meaning of the name "organic compound"?
2. How may one account for the existence of so great a number of compounds containing the same few elements as found in the organic compounds?
3. What is meant by structural isomerism? Give examples to illustrate.
4. What are structural or graphic formulas?
5. What is meant by an homologous series of compounds? Write structural formulas for several members of the methane series of hydrocarbons.
6. What are the most noticeable differences in reactions between the paraffins and olefins? Illustrate by equations, using structural formulas to represent the compounds.
7. What is acetylene? What two methods are in use for its preparation? Give examples to indicate its importance in synthetic chemical industry.
8. What are diolefins? What two important methods may be used for the production of butadiene?
9. What is meant by polymerization? Which types of compounds readily undergo polymerization?
10. What is synthetic rubber? How may synthetic rubber be prepared?
11. How do the hydrocarbons of the benzene series differ from the paraffins and olefins?
12. What is the most important source of benzene and its homologues?
13. Write structural formulas for several of the homologues of benzene.
14. What is petroleum? Discuss the significance of the following processes in the

production of commercial products from petroleum: (*a*) fractional distillation; (*b*) cracking; (*c*) hydrogenation; (*d*) polymerization; (*e*) refining.

15. What is meant by the octane number of a gasoline?

16. What is tetraethyl lead? What is its function in ethyl gasoline?

SUPPLEMENTARY READINGS

Fuson, R. C., and H. R. Snyder, *Organic Chemistry*, John Wiley & Sons, Inc., New York, 1942, chaps. I–VI.

Conant, J. B., *The Chemistry of Organic Compounds*, The Macmillan Company, New York, 1939, chaps. III–IV, XVIII.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 14, 24, 39.

Frolich, P. K., "Petroleum — Past, Present, Future," *Ind. Eng. Chem.* **35**, 1131 (1943).

Brooks, B. T., "A New Phase of the Petroleum Industry," *Chem. Eng. News* **21**, 939 (1943).

Egloff, G., "Peacetime Values from a War Technology," *Chem. Eng. News* **21**, 141 (1943).

Fisher, H. L., "Synthetic Rubber," *Chem. Eng. News* **21**, 741 (1943).

Frolich, P. K., and C. E. Morrell, "Butadiene," *Chem. Eng. News* **21**, 1138 (1943).

Gamma, J. A., and T. Inouye, "Manufacture of Butadiene," *Chem. Met. Eng.* **49**, 12, 97 (1942); **50**, 1, 94 (1943).

Chapter 35

DERIVATIVES OF THE HYDROCARBONS

A large number of substances are classified as derivatives of the hydrocarbons. One or more of the hydrogen atoms of the hydrocarbon molecule is replaced by other atoms or groups of atoms in the formation of such compounds. Nevertheless, direct substitution is not the usual method for the production of the derivatives. These substances are further classified into groups of compounds that exhibit similarities in constitution and behavior. A particular group of atoms, known as a *functional group*, is characteristic of each of these classes of derivatives. The properties of a specific compound depend not only on the functional group it contains, but also on the nature of the organic radical that constitutes the remainder of the molecule. Radicals formed by removing an atom of hydrogen per molecule from the paraffin hydrocarbons are called *alkyl radicals*, e.g., methyl, CH_3, ethyl, CH_3CH_2, and propyl, $CH_3CH_2CH_2$. The radicals corresponding to aromatic hydrocarbons are *aryl radicals*, e.g., phenyl, C_6H_5. Some of the classes of derivatives contain more than one functional group and exhibit specific reactions that are due to each. Derivatives of the paraffin hydrocarbons, containing only one kind of functional group, are considered first.

Halogen Substitution Products. Substitution reactions of chlorine and bromine, but not iodine, with the hydrocarbons produce halogen substitution products. The reaction is called *halogenation*. This reaction occurs when a mixture of the gaseous hydrocarbon and the halogen is exposed to sunlight and produces a mixture of products. The structural formulas of the chlorine substitution products of methane are:

$$
\begin{array}{ccccc}
\text{H} & \text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} \\
| & | & | & | & | \\
\text{H—C—H,} & \text{H—C—H,} & \text{H—C—Cl,} & \text{H—C—Cl,} & \text{Cl—C—Cl} \\
| & | & | & | & | \\
\text{H} & \text{H} & \text{H} & \text{Cl} & \text{Cl}
\end{array}
$$

| Methane | Chloro-
methane | Dichloro-
methane | Trichloro-
methane | Tetrachloro-
methane |
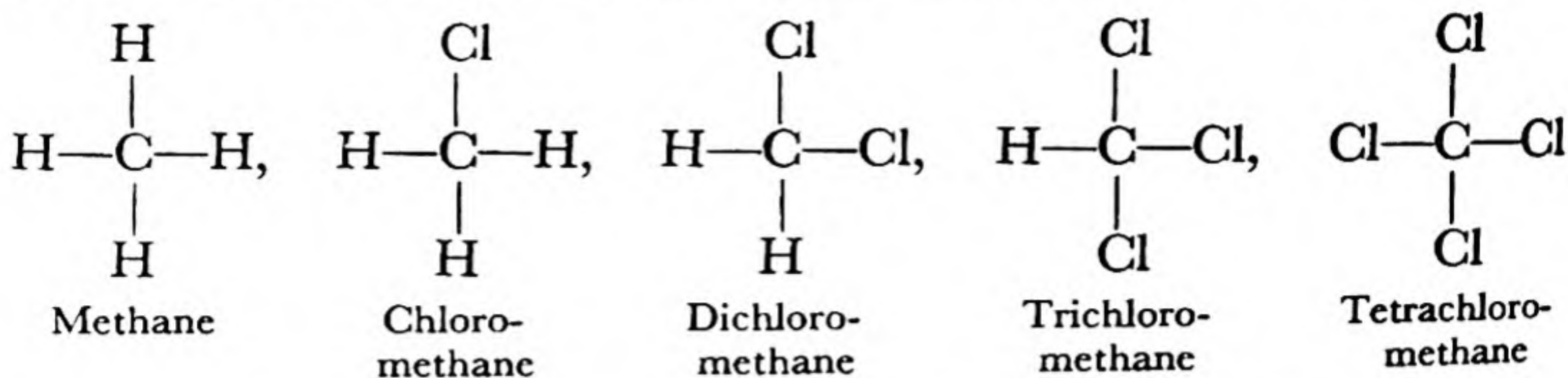
Monochloromethane, CH_3Cl, is commonly called methyl chloride, trichloromethane is chloroform, and tetrachloromethane is carbon tetrachloride. Some of these products have important direct uses, e.g., methyl chloride as a refrigerant, chloroform as an anaesthetic and as a solvent, and carbon tetrachloride as a solvent and in some types of fire extinguishers. Direct substitution is not employed commonly for the production of these substances, because the stage to which the reaction proceeds cannot be controlled. Methyl chloride may be prepared by the reaction of methanol, methyl alcohol, with hydrochloric acid; carbon tetrachloride, by the reaction of chlorine with carbon disulfide; and chloroform, by the reduction of carbon tetrachloride with moist finely divided iron. In general, the halogen substitution products of the paraffin hydrocarbons may be prepared by the reaction of the hydrogen halide or of phosphorus trichloride with the appropriate alcohol.

The Alcohols. The alcohols are members of a class of compounds containing the hydroxide group attached to aliphatic hydrocarbon molecules in place of hydrogen atoms. Only one hydroxide derivative of methane is known and two of ethane. From this, and other considerations, it is concluded that only one hydroxide group may be held normally in combination by a particular carbon atom in the molecule. Alcohols containing one hydroxide group are *monohydric alcohols*.

$$
\begin{array}{cc}
\text{H} & \text{H H} \\
| & |\ \ | \\
\text{H—C—OH} & \text{H—C—C—OH} \\
| & |\ \ | \\
\text{H} & \text{H H}
\end{array}
$$

| Methyl Alcohol
Methanol | Ethyl Alcohol
Ethanol |
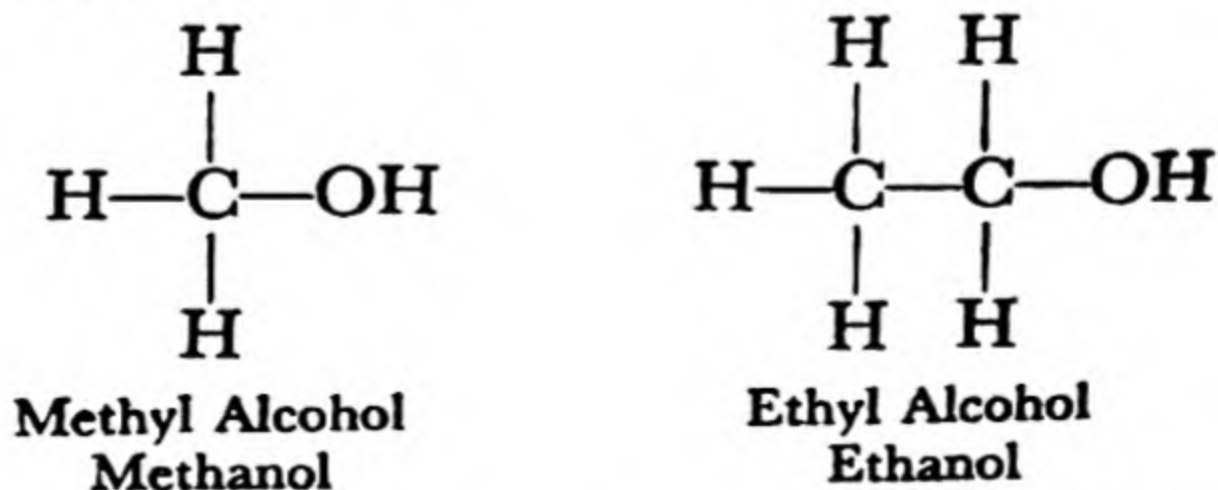
An alcohol in which the hydroxide group is attached to a terminal carbon in a straight chain compound is the *normal* or *primary* alcohol.

The primary alcohols are represented by the type formula, R—OH, in which R represents an alkyl radical. Two monohydric alcohols are possible if the hydrocarbon contains more than two atoms of carbon. The second isomeric alcohol contains the functional group attached to a carbon atom which is itself bound to two other atoms of carbon. It is called the *iso-* or *secondary* alcohol, and may be represented by the type formula R_2CHOH. When the hydroxide group is attached to a carbon atom bonded to three other atoms of carbon, the product is known as a *tertiary* alcohol, with the type formula R_3COH. These relationships are illustrated by the following formulas.

$$
\begin{array}{ccc}
\overset{\displaystyle H\ \ H\ \ H}{\underset{\displaystyle H\ \ H\ \ H}{H-C-C-C-O-H}} &
\overset{\displaystyle H\ \ H\ \ H}{\underset{\displaystyle H\ \ OH\ H}{H-C-C-C-H}} &
\overset{\displaystyle H\ \ CH_3}{\underset{\displaystyle H\ \ CH_3}{H-C-C-O-H}}
\end{array}
$$
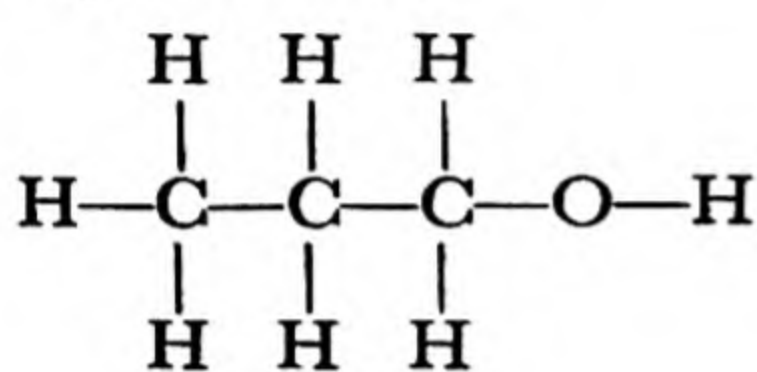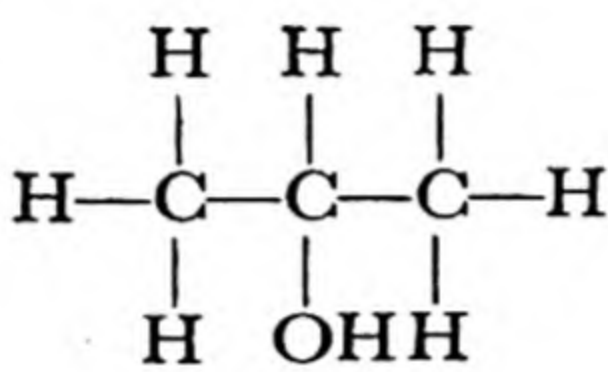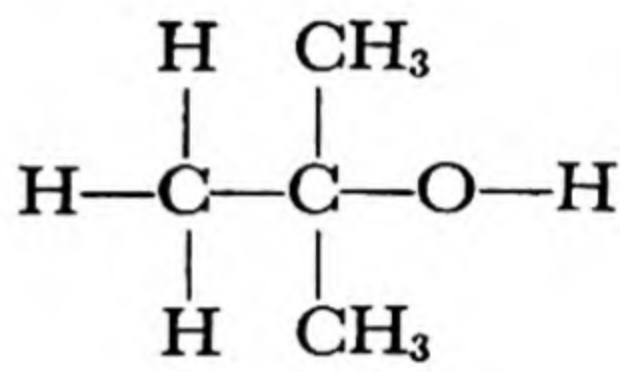
| Primary | Secondary | Tertiary |
| n-Propyl Alcohol | Isopropyl Alcohol | Butyl Alcohol |

The hydrogen atom of the hydroxide group may be displaced by sodium or by potassium to form an alkoxide. The product with ethanol is the ethoxide.

$$2\,C_2H_5OH + 2\,Na \longrightarrow 2\,C_2H_5ONa + H_2$$

The alcohols react with acids to form products known as esters.

$$C_2H_5OH + HNO_3 \longrightarrow C_2H_5NO_3 + H_2O$$

They also react with the trihalides of phosphorus to form the halogen substitution product.

$$3\,C_2H_5OH + PBr_3 \longrightarrow 3\,C_2H_5Br + H_3PO_3$$
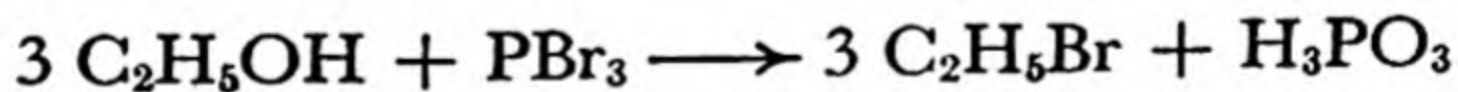
They may be dehydrated to form unsaturated hydrocarbons, and ethers. Alcohols may be oxidized to form aldehydes and acids.

Methyl alcohol, methanol, CH_3OH, also called wood alcohol, is a product of the destructive distillation of wood. Acetic acid, water, acetone, and other substances are produced during this process, so that it is necessary to separate wood alcohol from these other condensed products. Formerly, this was the only industrial source of methanol, but synthetic processes, which now yield a large portion of the world supply, have been developed. Methanol

is synthesized by the reaction of carbon monoxide and hydrogen at a pressure of approximately 200 atmospheres and a temperature of 300–400° in the presence of a contact catalyst such as a mixture of oxides of zinc and chromium, Fig. 135.

$$CO + 2 H_2 \rightleftharpoons CH_3OH$$
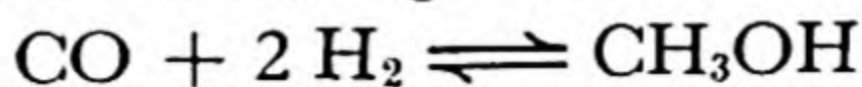
The gas mixture of the proper composition is prepared from water gas by the introduction of additional hydrogen. The reaction, yielding methanol, is reversible and exothermic, and favorable
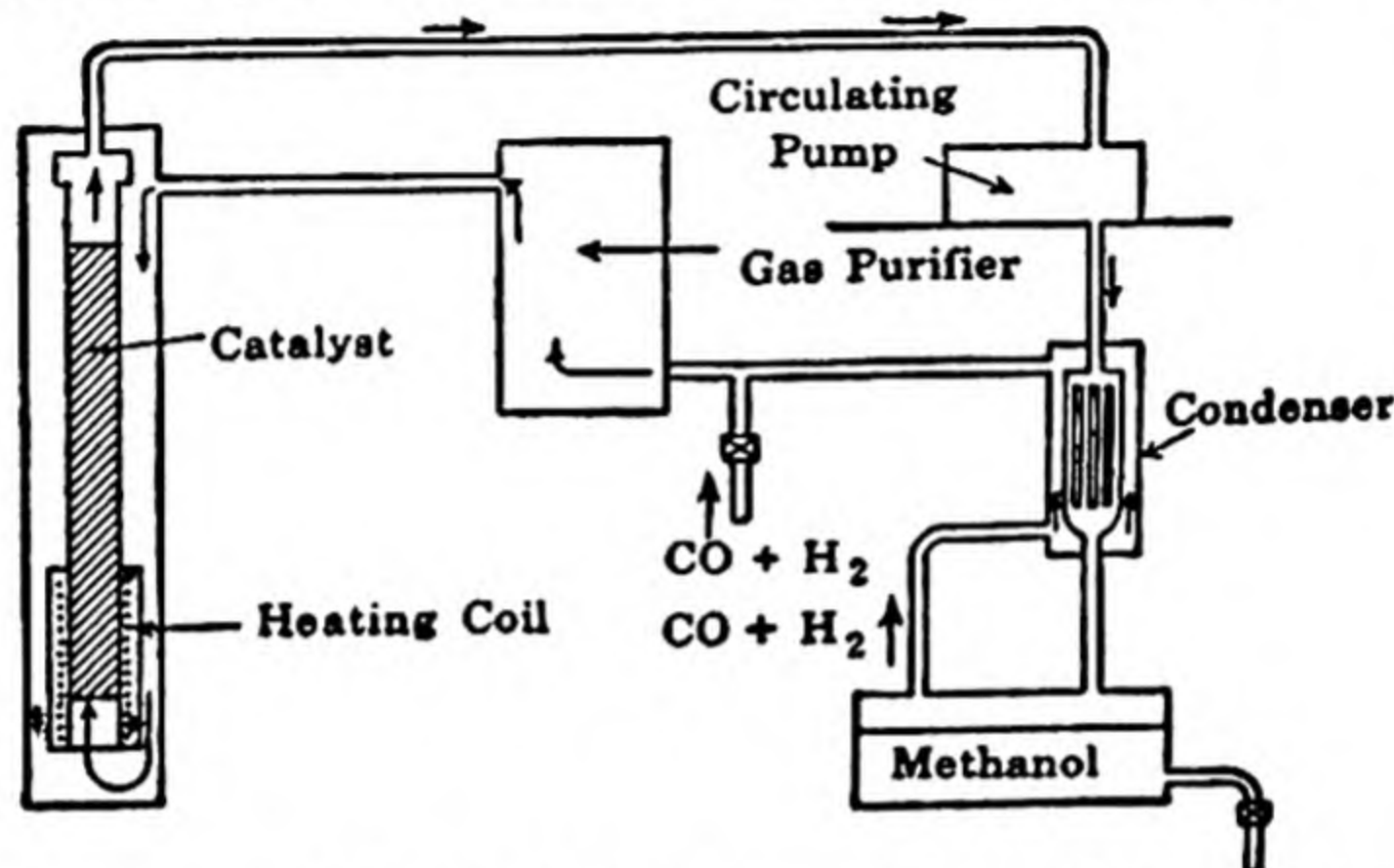
Fig. 135. *Diagram of Synthetic Methanol Process* (From Conant. *The Chemistry of Organic Compounds*)

conditions depend on the same factors as in the synthesis of ammonia. (See page 340.)

Methanol is a colorless liquid with a boiling point of 64.6°. It burns with a pale-blue flame, and the reaction is highly exothermic. Methanol is a poisonous substance. Small quantities taken internally often cause blindness, and larger quantities, death. It has been used as a denaturant for grain alcohol to make it unsuitable for beverage use and thus permit its sale, free from tax, for industrial uses. The boiling points of methanol and ethanol are near enough to each other to prevent a satisfactory separation by simple distillation. Methanol is used extensively for the production of formaldehyde.

Ethyl alcohol, ethanol, C₂H₅OH, is commonly produced by the fermentation of sugar and starch under the influence of certain enzymes. These enzymes are substances which are produced in the growth of microorganisms such as yeast. The reactions which occur during fermentation are catalyzed by the enzymes. Yeast

produces the two enzymes required for the fermentation of cane sugar. In the presence of *invertase*, cane sugar is converted into a mixture of the two isomeric sugars, glucose and fructose, by an addition reaction with water.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
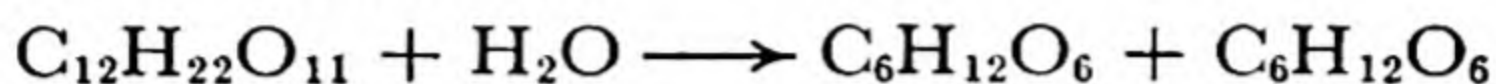
In the presence of *zymase*, these substances decompose to form ethyl alcohol and carbon dioxide.

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$$
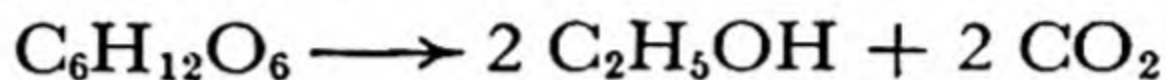
The fermentation of starch requires the action of the enzyme *diastase*, which is formed when barley begins to sprout in a warm, damp atmosphere. In the presence of diastase in malt produced from barley, starch first yields maltose, an isomer of cane sugar, and this sugar ferments in the presence of yeast. *Industrial alcohol* is usually produced by fermentation, in concentrations up to about 10 per cent. Yeast grows more slowly as the concentration of the alcohol becomes greater, and ceases to grow altogether at about 15 per cent. The dilute solution may be concentrated by fractional distillation to produce the constant boiling solution containing 95.5 per cent of alcohol. Pure ethanol, known as absolute alcohol, cannot be obtained by distillation of the aqueous solution, but may be prepared by the addition of calcium oxide to react with water, followed by the distillation of alcohol from the lime. Absolute alcohol is produced industrially by the fractionation of solutions of 95.5 per cent ethanol containing regulated proportions of benzene. A mixture of water, alcohol, and benzene distills first and then a mixture of alcohol and benzene. After all of the water and benzene have been removed, pure ethanol is obtained.

Ethanol is a colorless liquid with a boiling point of 78.5°. It is soluble in water in all proportions. It is a valuable solvent for many substances that do not dissolve in water. Its use as a solvent in the production of suitable forms of explosives has led to a tremendous increase in demand during war. It is also used in large quantities as a chemical intermediate in the production of many other materials, such as ethylene, ether, and butadiene. Large quantities of alcohol are used in antifreeze solutions in automobile radiators.

Ethylene glycol, CH₂OHCH₂OH, is the simplest of the dihydric alcohols. It is produced from ethylene by reaction with chlorine

water to form ethylene chlorhydrin. This substance is then heated with sodium bicarbonate solution to form ethylene glycol.

$$H-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H + HOCl \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-H$$

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-H + HCO_3^- \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-H + CO_2 + Cl^-$$
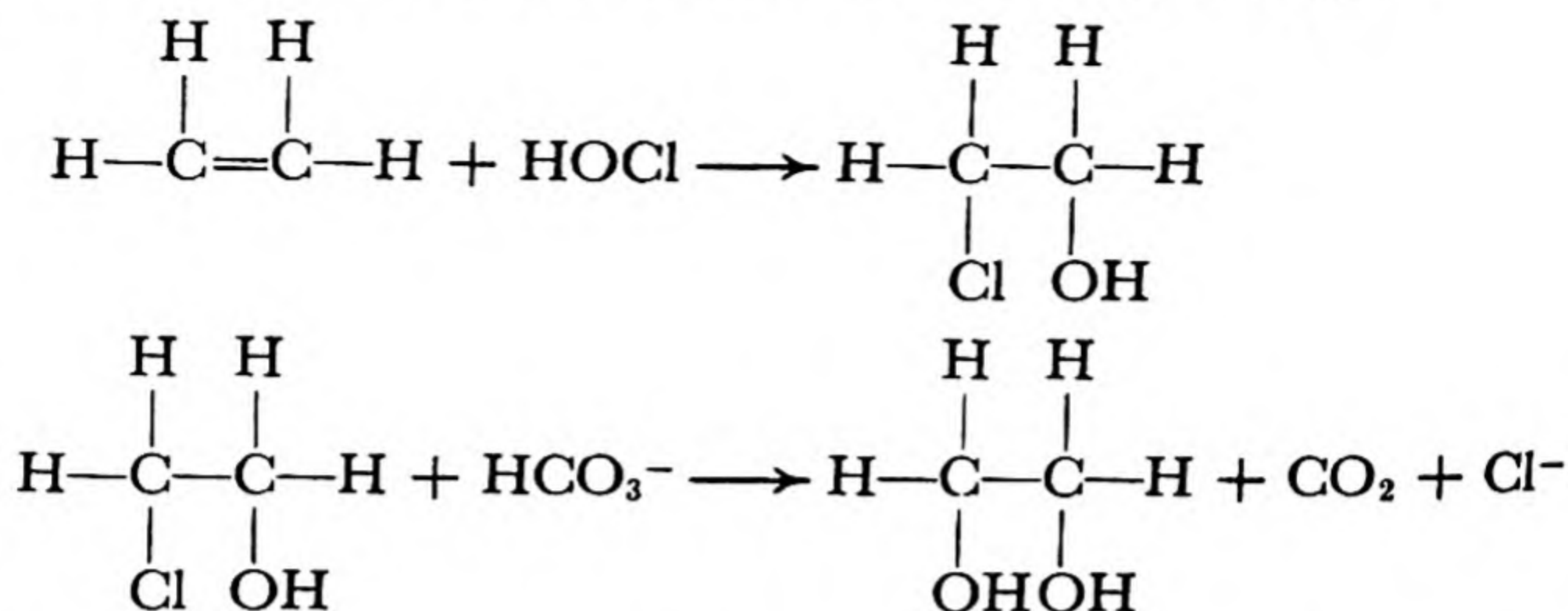
It is soluble in water in all proportions and has a boiling point of 197°. It is used in large quantities as an antifreeze in preference to methanol and ethanol, because of its lower volatility.

Glycerine, glycerol, **CH₂OHCHOHCH₂OH,** is the simplest of the trihydric alcohols. It is a by-product of the manufacture of soap from animal and vegetable fats and oils by reaction with an alkali metal hydroxide. It is highly soluble in water and is used to some extent in tobacco to absorb moisture from the air and thus prevent the tobacco from becoming too dry. It is also used in cosmetics and in cellophane. The principal use of glycerol is in the production of glyceryl trinitrate for use in explosives.

The Ethers. The ethers are members of an important class of compounds containing two alkyl radicals in combination with an atom of oxygen. They may be represented by the type formula, R—O—R′, in which R and R′ may be the same or may be different radicals. Ethyl ether, commonly called ether, is prepared by the dehydration of ethanol by sulfuric acid at 130–140°.

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\boxed{O-H + H}-O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \longrightarrow$$

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H + H_2O$$
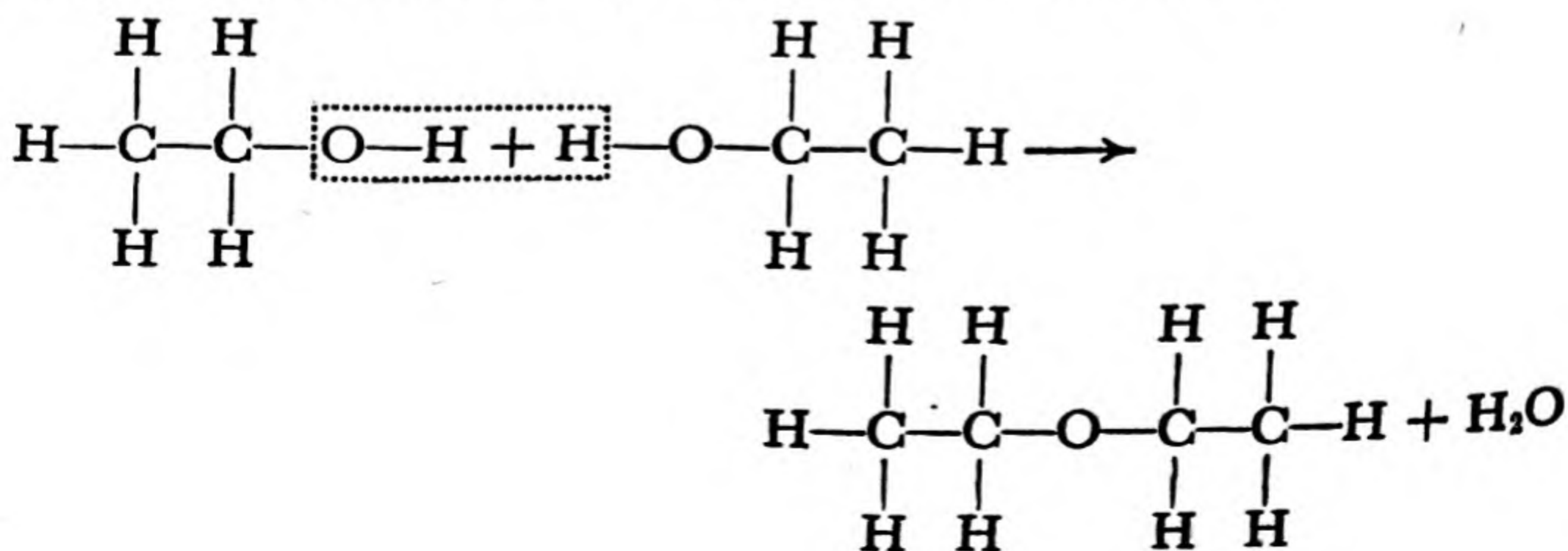
It is also prepared by the dehydration of ethanol over aluminum oxide at 250–300°. Ethyl ether is a colorless, volatile liquid boiling at 34.6°. It is the most widely used general anaesthetic. It is a valuable solvent, which has low solubility in water. A large number of synthetic products are soluble in ether, and an important use of ether is for the extraction of such materials from aqueous solutions. Other ethers may be prepared by similar reactions. Mixed ethers, in which R and R′ are different radicals, may be prepared from two different alcohols. One of the alcohols is converted into the halide by reaction with the hydrohalic acid, and the other into the alkoxide by reaction with sodium. These products react with each other to form the ether.

$$ROH + HCl \longrightarrow RCl + H_2O$$
$$2\,R'OH + 2\,Na \longrightarrow 2\,R'ONa + H_2$$
$$RCl + R'ONa \longrightarrow ROR' + NaCl$$
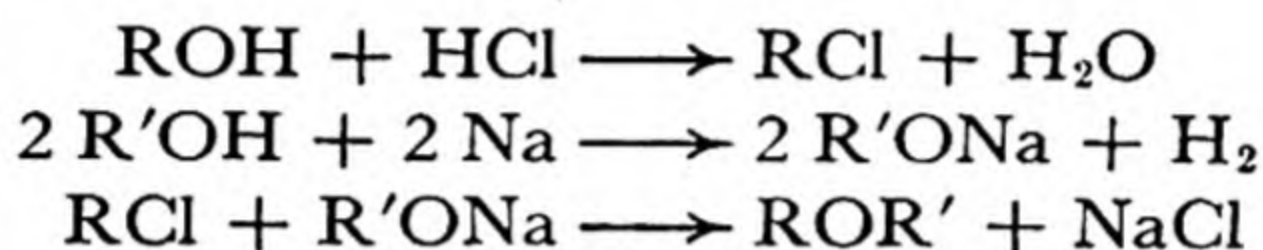
The Aldehydes. The mild oxidation of a primary alcohol yields an aldehyde. Aldehydes may also be prepared by the catalytic dehydrogenation of the alcohol. Two hydrogen atoms are removed from a molecule of the alcohol in this reaction, one from the hydroxide group and the other from attachment to the carbon atom that holds the hydroxide group. Consequently, the aldehyde contains the functional group

$$-\overset{\displaystyle H}{\underset{\displaystyle |}{C}}=O,$$

and may be represented by the type formula, RCHO, in which R represents hydrogen or an alkyl radical. Aldehydes are named from the acid formed by the oxidation of the aldehyde. They are also named by the use of the suffix -al, replacing the suffix -ol in the name of the alcohol. Thus, the aldehyde having the formula HCHO is called formaldehyde and also methanal. The formulas of the first three members of the series are:
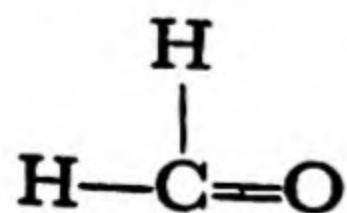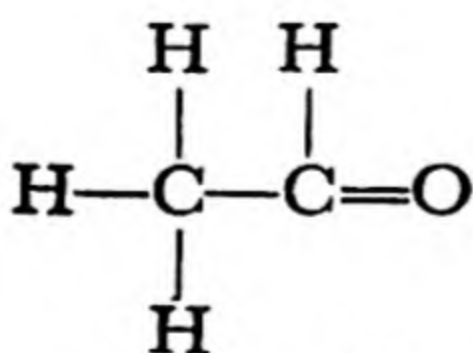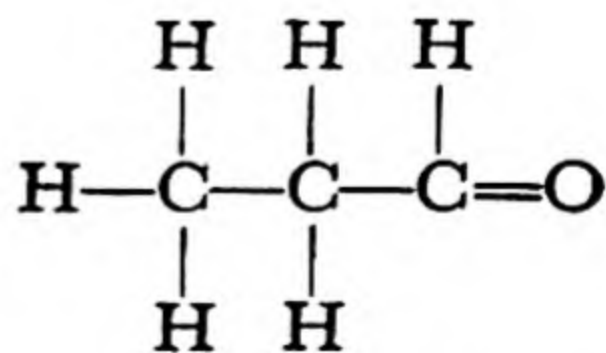
| Formaldehyde | Acetaldehyde | Propaldehyde |
| Methanal | Ethanal | Propanal |

Formaldehyde, methanal, **HCHO,** is prepared by mild oxidation and dehydrogenation when a mixture of air and methanol is passed over copper gauze at 300°.

$$2\,CH_3OH + O_2 \longrightarrow 2\,HCHO + 2\,H_2O$$
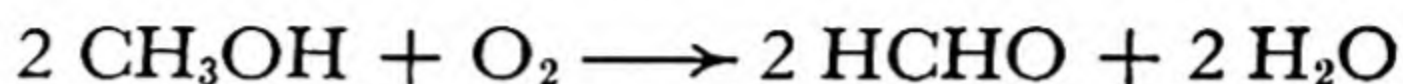
The boiling point of formaldehyde is − 21°. The 40 per cent solution, *formalin*, is used as a disinfectant and as a preservative for biological specimens. Formaldehyde polymerizes to form the solid condensation product known as paraformaldehyde. The aldehyde group is altered during polymerization, and the product does not exhibit the typical aldehyde reactions. However, it decomposes to form gaseous formaldehyde when heated. Formaldehyde also yields condensation products with other substances, producing resins which have great industrial importance as plastics, *e.g.,* Bakelite.

Acetaldehyde, ethanal, **CH₃CHO,** may be formed by oxidation and dehydrogenation of ethanol. Large quantities of acetaldehyde are produced by the catalytic hydration of acetylene in the presence of an acidic solution of mercuric sulfate as a catalyst. (See page 557.) Acetaldehyde boils at 21°. In the presence of sulfuric acid, it is converted into the polymer, paraldehyde, which boils at 124°. Acetaldehyde is readily oxidized to acetic acid and reduced to ethanol.

The Ketones. Ketones are produced by mild oxidation and by dehydrogenation of secondary alcohols. Ketones contain the functional group $>\!C\!=\!O$, known as the carbonyl group. They may be represented by the type formula RR′CO, in which R and R′ may or may not be the same alkyl radical. Acetone may be prepared from isopropyl alcohol.

$$
\begin{array}{ccccccccc}
\text{H} & \text{H} & \text{H} & & & \text{H} & & \text{H} \\
| & | & | & & & | & & | \\
\text{H}\!-\!\text{C}\!-\!\text{C}\!-\!\text{C}\!-\!\text{C} & \xrightarrow[\text{Cu}]{300°} & \text{H}\!-\!\text{C}\!-\!\text{C}\!-\!\text{C}\!-\!\text{H} + \text{H}_2 \\
| & | & | & & & | & \| & | \\
\text{H} & \text{OH} & \text{H} & & & \text{H} & \text{O} & \text{H}
\end{array}
$$
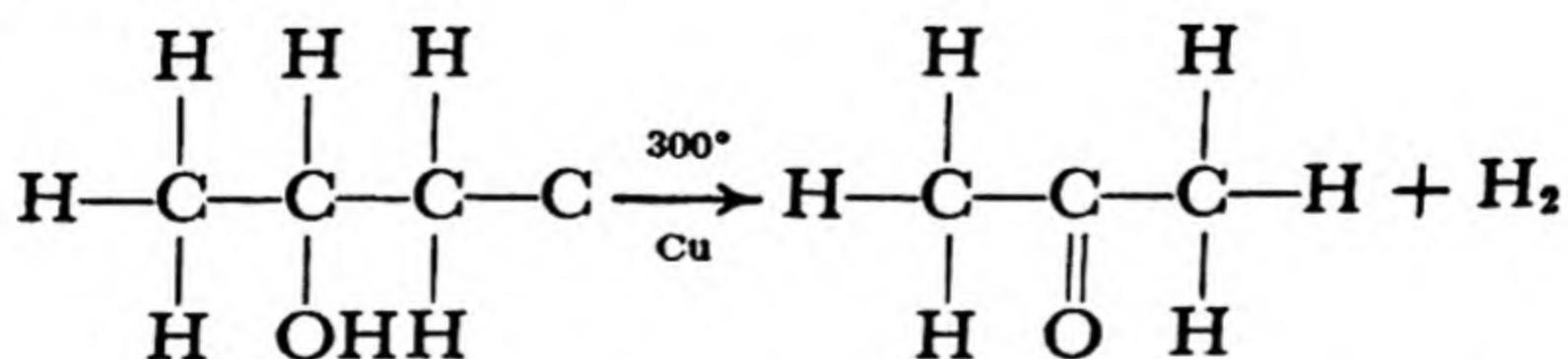
Acetone is a product of the destructive distillation of wood and is also prepared from calcium acetate, obtained from acetic acid formed during the wood distillation.

$$Ca(C_2H_3O_2)_2 \longrightarrow CaCO_3 + CH_3COCH_3$$
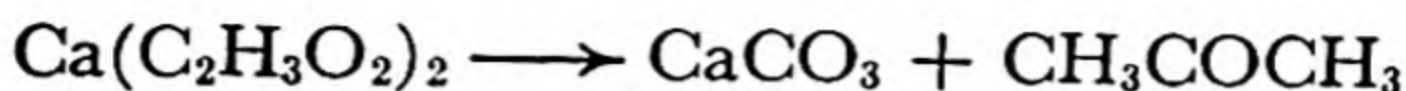
It is also produced from molasses and from corn by fermentation in the presence of the bacterium, *Clostridium acetobutylicium*. The products are about 60 per cent *n*-butanol, 30 per cent acetone, and 10 per cent ethanol. Acetone is an important solvent.

The Acids. The simple organic acids contain the carboxyl group, —COOH, which may split off the proton to form hydronium ions in solution. The acids corresponding to the paraffin hydrocarbons may be represented by the type formula RCOOH, R representing an atom of hydrogen or an alkyl radical. These acids are sometimes called fatty acids, because compounds of some of the higher homologues in the series are fats. The structure of the carboxyl group is represented in the formulas of the following acids.
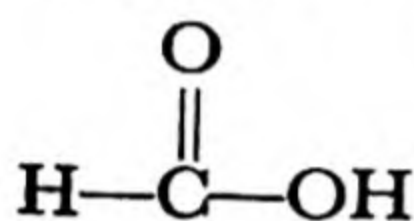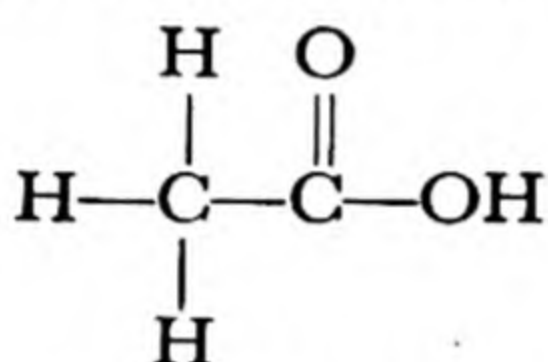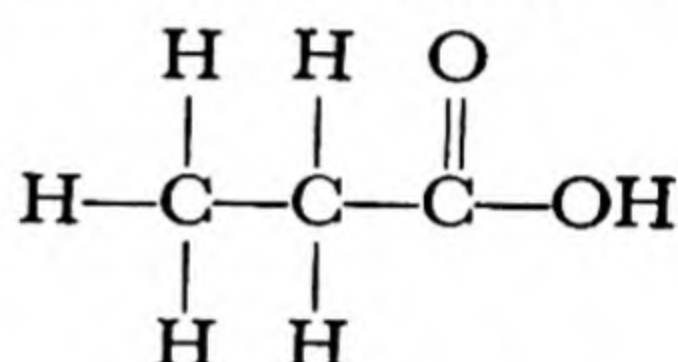
<pre>
      O   H O   H H O
      || | || | | ||
 H—C—OH   H—C—C—OH   H—C—C—C—OH
                      | | |
                      H   H H

  Formic Acid   Acetic Acid   Propionic Acid
</pre>

These acids are weakly ionized and exhibit the usual properties of weak acids.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
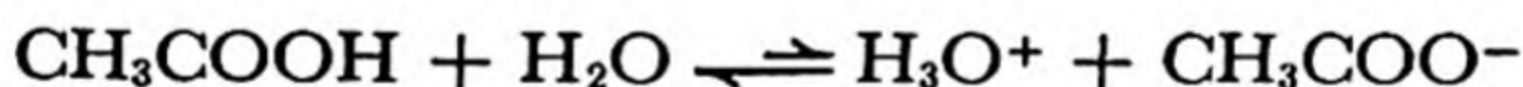
The acids may be prepared by oxidation of the alcohols and the aldehydes, and by acid hydrolysis of the organic cyanides.

$$CH_3CN + 2\,H_3O^+ + SO_4^{--} \longrightarrow CH_3COOH + NH_4^+ + HSO_4^-$$
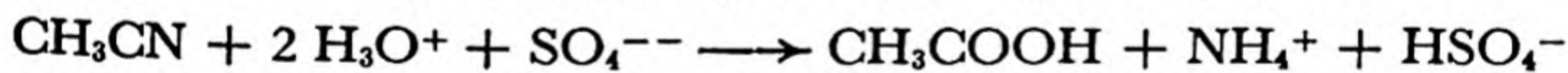
Formic acid, **HCOOH**, is found in nettles and in red ants. It is commonly prepared by first forming sodium formate as the product of the reaction of carbon monoxide with concentrated solutions of sodium hydroxide at a temperature of 150° and a pressure of 15 atmospheres.

$$CO + NaOH \longrightarrow HCOONa$$
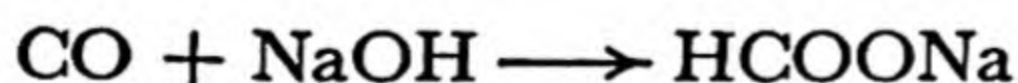
Sodium formate reacts with sulfuric acid, producing formic acid.

$$2\,HCOONa + H_2SO_4 \longrightarrow 2\,HCOOH + Na_2SO_4$$
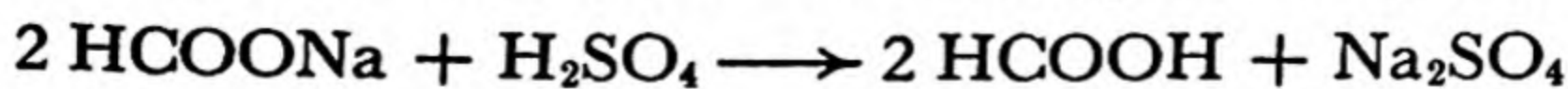
If an excess of concentrated sulfuric acid is added to sodium formate, formic acid is dehydrated, producing carbon monoxide.

Acetic acid, **CH₃COOH,** is prepared by the destructive distillation of wood and by the fermentation of ethanol. It is also prepared industrially in large quantities by the atmospheric oxidation of acetaldehyde, using manganous oxide as a catalyst.

$$2\ CH_3CHO + O_2 \longrightarrow 2\ CH_3COOH$$
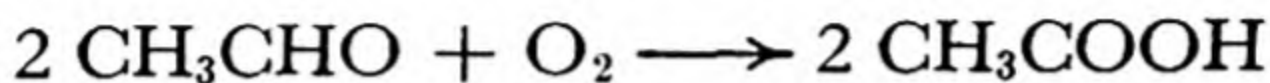
Acetic anhydride, $(CH_3CO)_2O$, may be prepared by the reaction of acetylene with acetic acid, using mercuric sulfate as a catalyst. The direct product of the reaction decomposes when heated, forming acetic anhydride and acetaldehyde.

$$C_2H_2 + 2\ CH_3COOH \longrightarrow (CH_3COO)_2CHCH_3$$
$$(CH_3COO)_2CHCH_3 \longrightarrow (CH_3CO)_2O + CH_3CHO$$
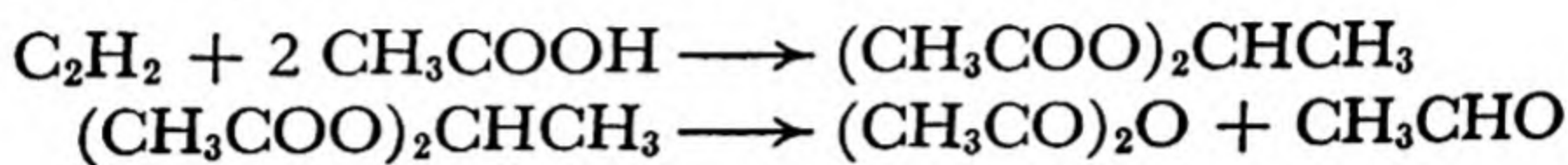
Acetic acid and the anhydride are used extensively in the formation of such products as cellulose acetate.

The Acid Chlorides. Acid chlorides, also called *acyl chlorides,* may be prepared by the replacement of the hydroxide group of the acid by chlorine. They are represented by the type formula RCOCl. The suffix *-yl* replaces the suffix *-ic* in the name of the acid. Thus, acetic acid has the formula CH_3COOH and acetyl chloride the formula CH_3COCl. The acyl chlorides may be prepared by the reaction of phosphorus trichloride with the acid.

$$3\ R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + PCl_3 \longrightarrow 3\ R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_3PO_3$$
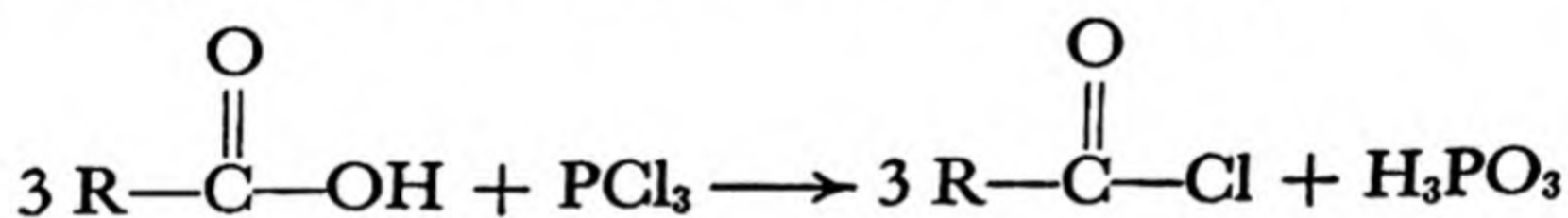
The acyl chlorides are hydrolyzed with the formation of the carboxylic acid and hydrochloric acid.

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$
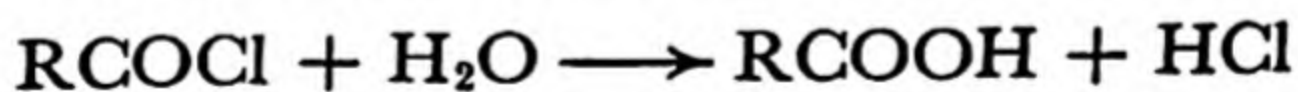
They also react with ammonia to form amides, and with alcohols to form esters.

The Amides. The amides are derivatives of acids, containing the $-NH_2$ group in place of the hydroxide group of the acid. They may be represented by the type formula $R-CONH_2$. They are readily prepared by the reaction of the acid chloride or the acid anhydride with ammonia.

$$CH_3COCl + 2\ NH_3 \longrightarrow CH_3CONH_2 + NH_4Cl$$
$$(CH_3CO)_2O + 2\ NH_3 \longrightarrow CH_3CONH_2 + CH_3COONH_4$$
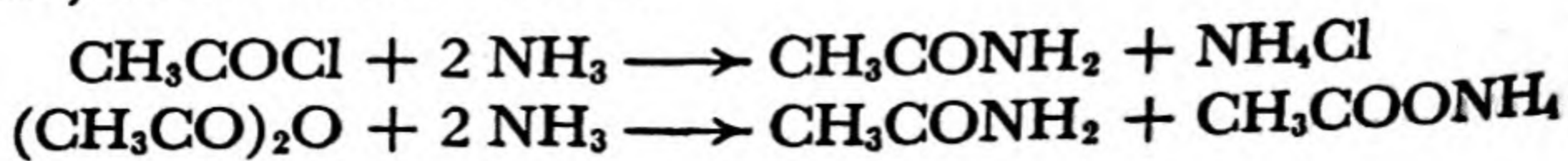
The amide derived from acetic acid is acetamide. It may also be prepared by the dehydration of ammonium acetate.

$$CH_3COONH_4 \longrightarrow CH_3CONH_2 + H_2O$$
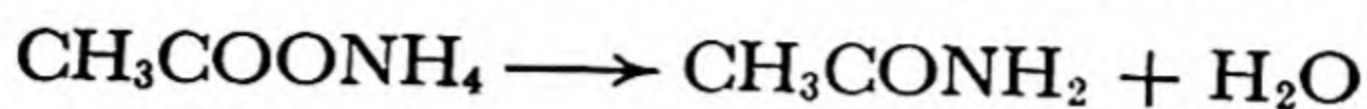
These compounds have important applications in the synthesis of other organic compounds.

The Esters. The esters make up a class of organic compounds, produced by the reaction of alcohols with acids. They are also prepared by the reaction of alcohols with acid chlorides and acid anhydrides. They may be represented by the type formula R—COOR'. The reaction of an alcohol with an acid, called *esterification*, involves the combination of the hydrogen of the functional group of the alcohol and the hydroxy group of the acid with the formation of water.
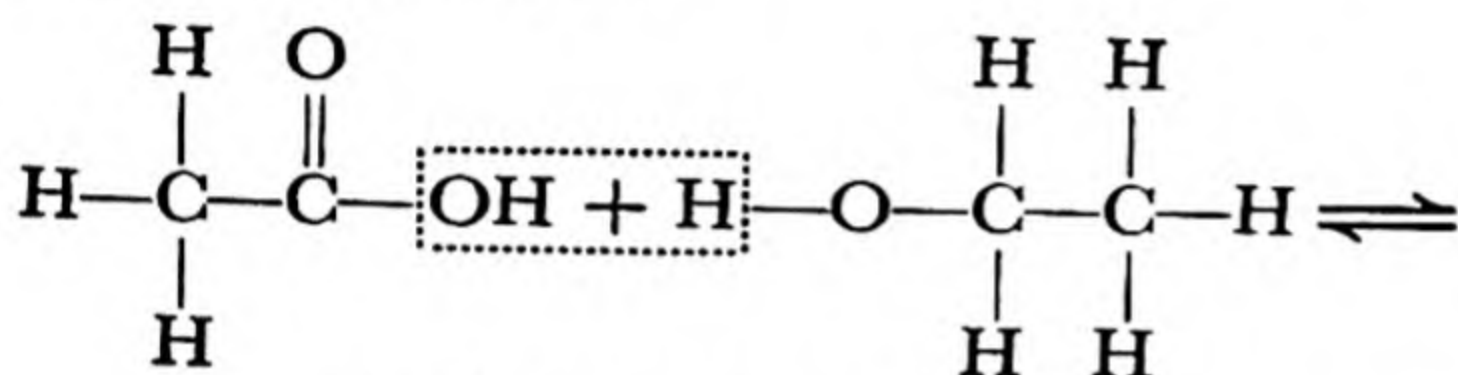
Acetic Acid + Ethanol
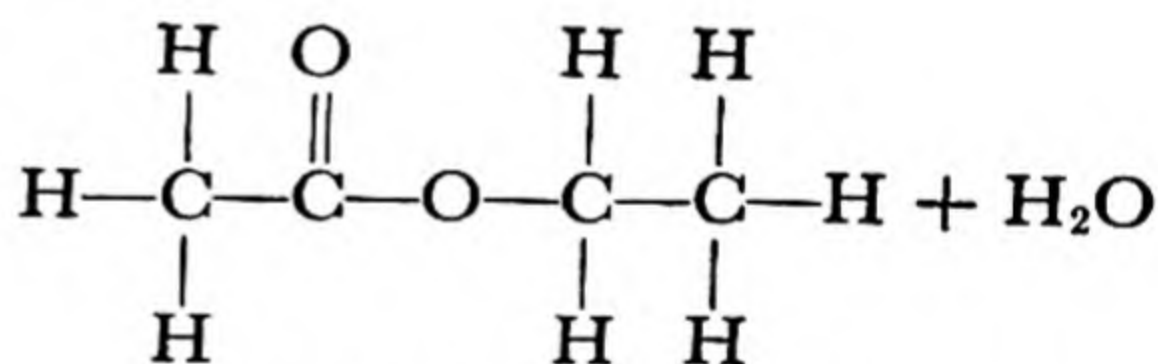
Ethyl Acetate (an Ester)

The rate of reaction is increased by the presence of mineral acids, *e.g.*, sulfuric acid. The reaction is reversible, and a state of equilibrium is established. The reverse reaction is the hydrolysis of the ester. The acid is neutralized in the presence of an excess of a basic hydroxide and the hydrolysis of the ester is completed. The reaction in which a strong base is employed with the decomposition of an ester into an alcohol and a salt is known as *saponification*.

Some of the esters have pleasant odors which cause the characteristic fragrance of fruits and flowers. Many of the esters are synthesized for use in perfumes and flavors. The natural odors of the flowers are usually due to a mixture of volatile esters, some of which are present in only small proportions. Therefore, the synthetic perfumes lack some of the constituents and fail to give

the true fragrance of the flower. The fats and oils are esters of the trihydric alcohol, glycerol, with certain organic acids of high molecular weight. A number of the esters are of great industrial importance, *e.g.*, glyceryl trinitrate in dynamite, cellulose trinitrate in guncotton, and cellulose acetate in rayon.

Fats and Oils. The animal and vegetable fats and oils are mixtures of the glyceryl esters of long-chain organic acids, *e.g.*, palmitic acid, $C_{15}H_{31}COOH$, stearic acid, $C_{17}H_{35}COOH$, oleic acid, $C_{17}H_{33}COOH$, and linoleic acid, $C_{17}H_{31}COOH$. Oleic acid is an unsaturated acid with one double bond at the middle of the chain, and linoleic acid has two double bonds, while palmitic and stearic acids are saturated. The glyceryl esters are tripalmitin, $(C_{15}H_{31}COO)_3C_3H_5$, tristearin, $(C_{17}H_{35}COO)_3C_3H_5$, triolein, $(C_{17}H_{33}COO)_3C_3H_5$, and trilinolein, $(C_{17}H_{31}COO)_3C_3H_5$. The structural relation of these compounds to glycerol is shown by the following formulas:

$$
\begin{array}{cc}
\text{H} & \text{O} \qquad \text{H} \\
| & \parallel \qquad | \\
\text{H—O—C—H} & \text{R—C—O—C—H} \\
| & \text{O} \\
\text{H—O—C—H} & \parallel \\
| & \text{R—C—O—C—H} \\
\text{H—O—C—H} & \text{O} \\
| & \parallel \\
\text{H} & \text{R—C—O—C—H} \\
& | \\
& \text{H}
\end{array}
$$
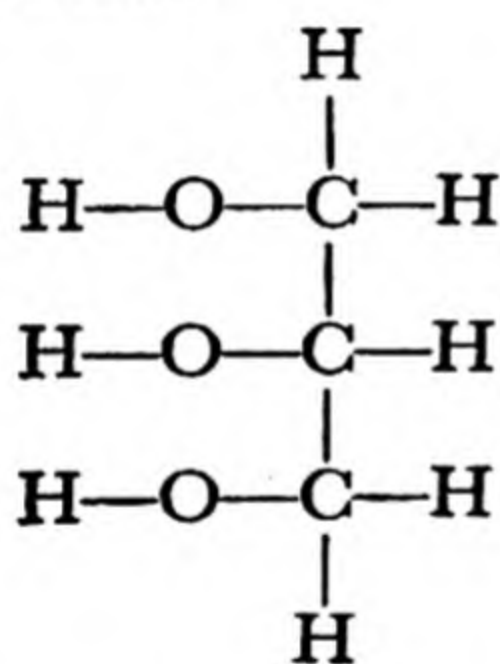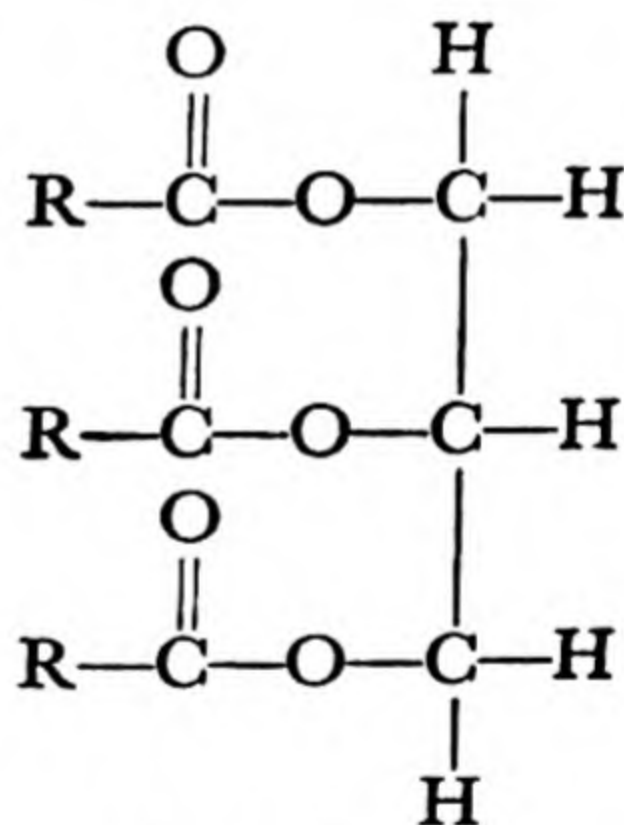
Glycerol   Glyceryl Ester

The melting points of these esters are: tristearin, 71°, tripalmitin, 60°, triolein, 17°, and trilinolein, − 6°. Consequently, natural products containing large percentages of triolein and trilinolein are liquid at ordinary temperatures, *e.g.*, olive oil which contains about 70 per cent of triolein, 5 per cent of trilinolein, and 25 per cent of tripalmitin and tristearin together, and cotton seed oil which contains 25 per cent of triolein, 47 per cent of trilinolein, 25 per cent of tripalmitin and tristearin together, and 3 per cent of other glycerides. Beef tallow contains 75 per cent of tripalmitin and tristearin, with 25 per cent of triolein. Butter contains about 53 per cent of tripalmitin and tristearin, 39 per cent of triolein, 2–3 per

cent of tributyrin, $(C_3H_7COO)_3C_3H_5$, with small percentages of other glycerides. The hydrolysis of tributyrin produces butyric acid, which has the disagreeable odor noticed in rancid butter.

The catalytic hydrogenation of vegetable oils, such as cotton seed oil and soy bean oil, converts the unsaturated esters into saturated products. This may be accomplished by passing hydrogen through the oil at a temperature about 200° in the presence of nickel as a catalyst. The complete hydrogenation of triolein and trilinolein converts them into tristearin, a hard waxlike product. In order to obtain a fat of the desired consistency, hydrogenation may be discontinued when the right proportion of saturated esters has been formed. The properly hydrogenated product has the same calorific value as butter, but lacks small percentages of esters of lower fatty acids, so that there is a difference in flavor.

Linseed oil — containing about 30 per cent each of the glyceryl esters of linoleic acid and of a still less saturated acid, linolenic acid, $C_{17}H_{29}COOH$ — and tung oil — containing about 73 per cent of the glyceryl ester of eleostearic acid which is isomeric with linolenic acid — become oxidized when exposed to air. Raw linseed oil absorbs oxygen very slowly, but it undergoes a change when heated at 200° in the presence of certain inorganic materials, so that it will subsequently absorb oxygen more rapidly and " dry " more quickly. The oxidation of these products forms a hard, tough, transparent film. These oils serve as the vehicle in paint. (See page 481.) They are also used in the manufacture of oilcloth and linoleum.

Soap. The soaps are salts of higher fatty acids. The common soaps are sodium salts soluble in water. Soaps are prepared by heating the fat or oil of proper composition with sodium hydroxide or potassium hydroxide. The saponification of the fat or oil produces glycerol and the salt of the fatty acid. The reaction of triolein with sodium hydroxide produces sodium oleate.

$$(C_{17}H_{33}COO)_3C_3H_5 + 3\,NaOH \longrightarrow C_3H_5(OH)_3 + 3\,C_{17}H_{33}COONa$$
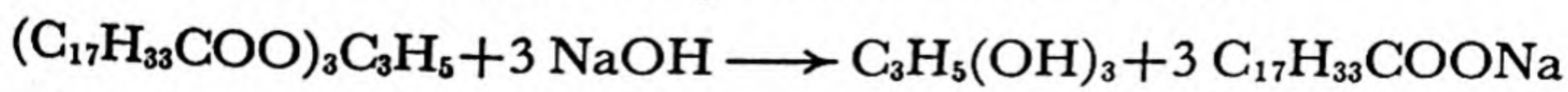
After the reaction is complete, common salt is added to coagulate the soap, which rises to the surface and is removed. Glycerol is separated from the brine by distillation.

The composition of the soap depends on the composition of the

fat or oil and of the base used in saponification. The potassium soaps are more soluble than the corresponding sodium compounds. Liquid soaps are commonly prepared by using potassium hydroxide in the saponification of fats and oils containing large percentages of triolein. Other substances are added to produce soaps for special purposes. Naphtha soaps contain emulsified petroleum naphtha, which is a solvent for fats and oils. Medicated soaps contain antiseptics such as phenol. Floating soaps are aerated so that the product is less dense than water.

Calcium, magnesium, and iron soaps are insoluble. Consequently, hard water, which contains compounds of these elements in solution, reacts with the soluble soaps to produce a precipitate and thus cause great waste because these insoluble products have no cleansing action. Some of the insoluble soaps are useful in ointments, *e.g.*, lead, copper, and mercury soaps. Zinc stearate and zinc palmitate are used in face powder.

Hard water detergents are sodium salts of certain organic derivatives of sulfuric acid. They are known as sodium alkyl sulfates. They may be prepared by the reaction of long-chain alcohols with sulfuric acid to form the alkyl sulfuric acid. This product is then neutralized to form the salt. Lauryl alcohol, $CH_3(CH_2)_{19}CH_2OH$, which may be obtained from cocoanut oil, is used for this purpose. The sodium alkyl sulfates suitable for use as detergents may be represented by a general formula $CH_3(CH_2)_nCH_2OSO_3Na$. The iron, calcium, and magnesium salts of these acids are soluble in water. Hence, these detergents may be used in hard water and also in weakly acidic solutions.

The Amines. Derivatives of ammonia in which atoms of hydrogen have been replaced by alkyl or aryl radicals are amines. Primary amines in the aliphatic series contain one alkyl group, RNH_2. The $—NH_2$ group is called the amino group. The secondary amines contain two alkyl groups, R_2NH, and the tertiary amines, three such groups, R_3N. Amines may be prepared by a number of reactions; but no single method is generally applicable for the preparation of all amines. Many of the alkyl halides react with ammonia to form a mixture of primary, secondary, and tertiary amines. Ethyl chloride reacts with ammonia forming ethyl amine, diethyl amine, and triethyl amine.

$$CH_3CH_2Cl + 2\ NH_3 \longrightarrow CH_3CH_2NH_2 + NH_4Cl$$
$$2\ CH_3CH_2Cl + 3\ NH_3 \longrightarrow (CH_3CH_2)_2NH + 2\ NH_4Cl$$
$$3\ CH_3CH_2Cl + 4\ NH_3 \longrightarrow (CH_3CH_2)_3N + 3\ NH_4Cl$$
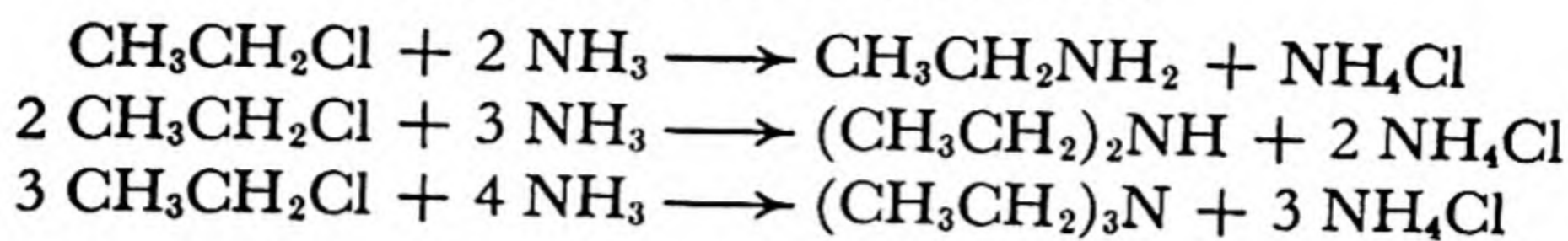
The boiling points of these products differ enough to permit separation by distillation. Primary amines, free from secondary and tertiary amines, may be prepared by converting the alkyl halide into the cyanide by reaction with sodium cyanide in alcohol solution, followed by reduction with hydrogen in contact with a catalyst.

$$CH_3CH_2Cl + NaCN \longrightarrow CH_3CH_2CN + NaCl$$
$$CH_3CH_2CN + 2\ H_2 \longrightarrow CH_3CH_2CH_2NH_2$$
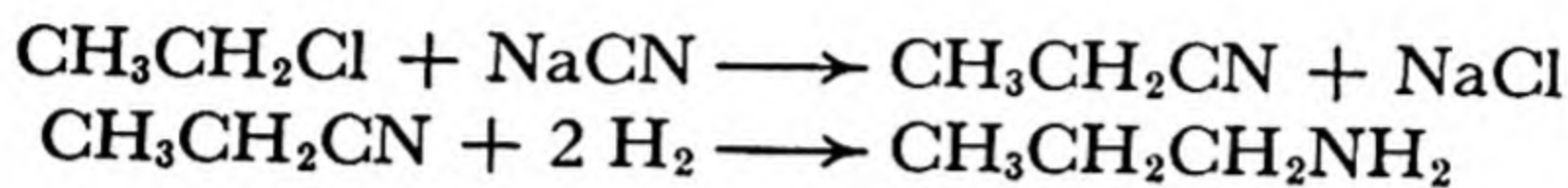
The alkyl radical of the next higher hydrocarbon is formed in this reaction.

The amines are basic in character, taking up protons to form substituted ammonium ions. Methyl amine is a stronger base than ammonia. It reacts with hydrochloric acid to form methyl ammonium chloride.

$$CH_3NH_2 + H^+ + Cl^- \longrightarrow CH_3NH_3^+ + Cl^-$$
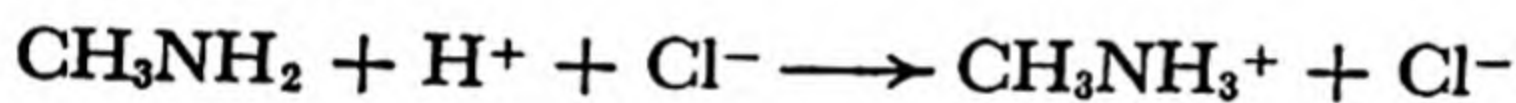
This product is commonly represented by the formula CH_3NH_2HCl, and is called methyl amine hydrochloride. The amines are important intermediate products in many organic synthetic processes.

The Carbohydrates. Some of the compounds of carbon, hydrogen, and oxygen contain the two latter elements in the same proportions as in water. Carbohydrates are formed in plants by the reaction of carbon dioxide and water in direct sunlight and in the presence of chlorophyll. The process is *photosynthesis* of the carbohydrates. The proportions in which these substances react to form glucose are:

$$6\ CO_2 + 6\ H_2O \longrightarrow C_6H_{12}O_6 + 6\ O_2$$
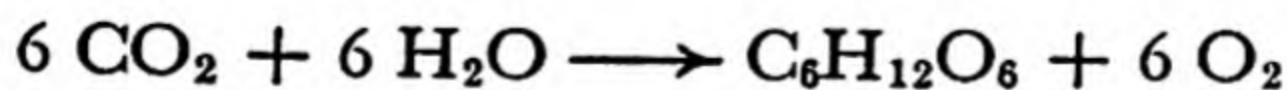
The proportions of water, involved in the formation of higher sugars, starch, and cellulose, are smaller.

The Sugars. There are two common classes of sugars, the monosaccharides and the disaccharides. *Glucose*, $C_6H_{12}O_6$, is the most common of the monosaccharides. It is also known as dextrose and as grape sugar. It occurs widely distributed in natural vegetable products and is prepared industrially by the hydrolysis of starch

in the presence of low concentrations of hydrochloric acid. *Fructose*, also known as fruit sugar, has the same empirical formula, and there are several isomers of these substances, known as *hexoses*. A general consideration of the properties of these substances indicates that they are polyalcohols and that glucose is also an aldehyde while fructose is a ketone.

Sucrose, *maltose*, and *lactose* are disaccharides with the empirical formula $C_{12}H_{22}O_{11}$. They are hydrolyzed in acidic solution and in the presence of enzymes to form two molecular proportions of monosaccharides.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
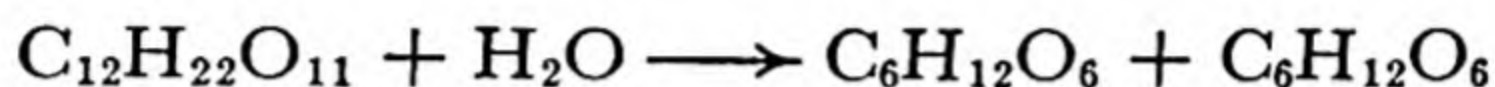
Sucrose, cane sugar, yields glucose and fructose; maltose, produced by the action of enzymes on starch, yields two molecular proportions of glucose; and lactose, milk sugar, yields glucose and another isomer called galactose.

Starch. Starch is a polysaccharide having the composition $(C_6H_{10}O_5)_x$. The hydrolysis of starch yields glucose, indicating that the molecules are composed of units with the glucose structure, but the number of these units in the molecule is not known. The cereal grains contain large percentages of starch, and potatoes contain about 20 per cent. When starch is treated with hot water, the granules burst, forming a colloidal suspension known as a *starch solution*. A deep blue color is produced when free iodine is added to a starch solution. The molecules break down to form smaller units when starch is heated to 200–250°. This product, known as *dextrin*, is soluble in cold water. It is used in the manufacture of the mucilage used on stamps and on gum tape. Through the action of the enzyme, *diastase*, starch hydrolyzes to form malt sugar which yields glucose by further hydrolysis.

Cellulose. The composition of cellulose is also represented by the empirical formula $C_6H_{10}O_5$. This substance is the most abundant of the carbohydrates. It is a constituent of all vegetable matter. The most important sources of cellulose products are cotton and wood. Lustrous fibers may be produced by converting cellulose or one of its derivatives into cylindrical fibers. These fibers may be spun and woven to form rayon. *The viscose process* is the most common process for the production of rayon. Cellulose is converted into

cellulose xanthate by reaction with sodium hydroxide and carbon disulfide. This product, disintegrated by water into a viscous mass, may be forced through minute circular orifices into a coagulating bath which removes the xanthate group, regenerating cellulose. *cellophane* may be formed by extruding the viscous material through a narrow slot into the coagulating bath. This product may be dyed in many colors and may be made moisture proof by coating it with a thin film of a lacquer.

Cellulose reacts with acids to produce cellulose esters. There are several nitrates of cellulose formed by reaction with a mixture of concentrated nitric and sulfuric acids. The highly nitrated product, containing 13.2–13.5 per cent of nitrogen is called *guncotton*. The partially nitrated material, *pyroxylin*, is prepared by regulating the concentration of the acids, the temperature, and the length of time allowed for the reaction. Pyroxylin is soluble in a mixture of ether and alcohol, forming a solution known as *Collodion*. The partially nitrated product is also soluble in other solvents. Solutions in butyl acetate, to which various other gums and resins are added, are extensively used as lacquers. Pyroxylin mixed with camphor yields a product known as celluloid, used in the production of photographic films. Pyroxylin is not explosive, but is very inflammable.

Cellulose acetate is made by the reaction of acetic anhydride with cellulose. This ester is soluble in a number of solvents. Films, which may be ignited only with difficulty, are made from cellulose acetate. These films are now used extensively in the motion picture industry. Cellulose acetate is used in one of the processes for the production of rayon. The product of this process is composed of esters of cellulose instead of regenerated cellulose as in the viscose process.

Derivatives of Aromatic Hydrocarbons. There are a number of classes of derivatives of aromatic hydrocarbons and many members in each class. Many of the derivatives prepared from homologues of benzene contain the functional group in the side chain. *The side chain* of an aromatic hydrocarbon is a group containing one or more atoms of carbon, attached to one of the carbon atoms of the benzene nucleus. Thus, toluene, $C_6H_5CH_3$, contains the methyl group as a side chain.

The side-chain derivatives include halides, alcohols, aldehydes, acids, and other substances similar to the corresponding derivatives of the paraffin hydrocarbons. The reactions of these substances are modified by the presence of the benzene nucleus in the molecule. The following formulas illustrate the structural relationships of several side-chain derivatives of toluene.

Benzyl Chloride   Benzyl Alcohol   Benzaldehyde   Benzoic Acid
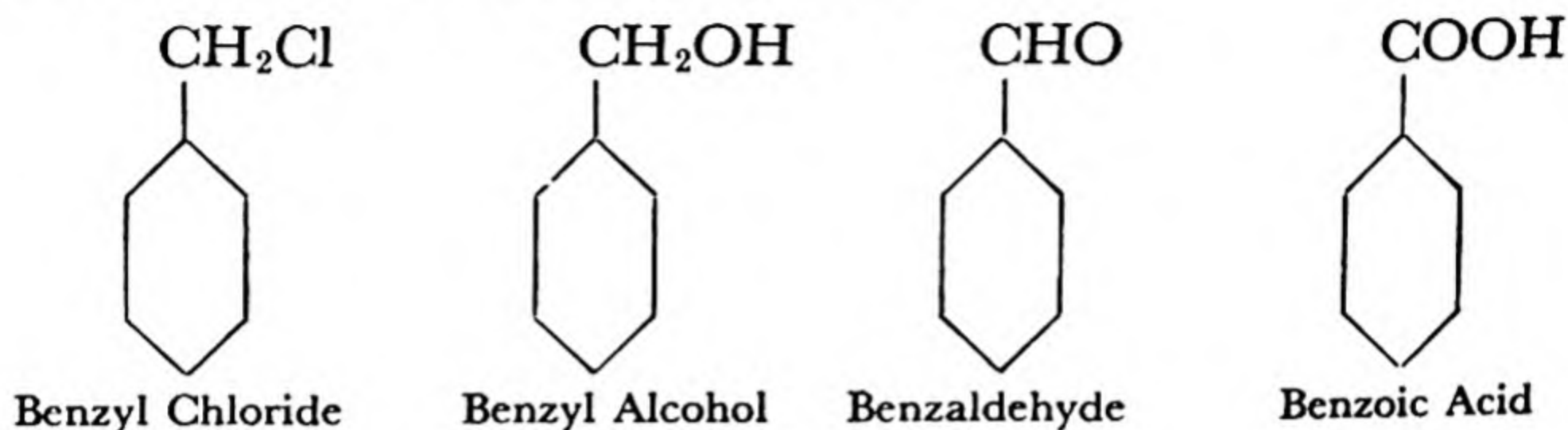
Aryl Halides. Chlorobenzene is prepared by the reaction of the halogen with warm benzene, using iron as a catalyst.
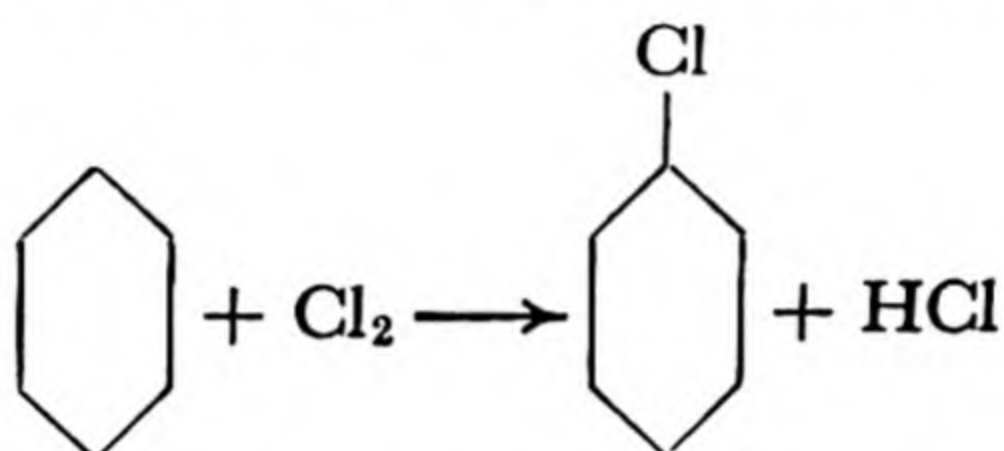
Bromine may also be substituted directly for hydrogen in the nucleus but iodine may not. If the reaction of chlorine with homologues of benzene takes place in the presence of ferric chloride as a catalyst, substitution of hydrogen atoms attached to nuclear carbon atoms occurs, but, if the reaction occurs in strong light, substitution is in the side chain. The aryl halides are not prepared by the reaction of the hydrohalic acid with the hydroxy derivatives of aromatic hydrocarbons. The aryl halides are less active than alkyl halides.

Sulfonic Acids. The reaction of the aromatic hydrocarbons with concentrated or fuming sulfuric acid may be used for the introduction of substituent groups into the nuclear structure.
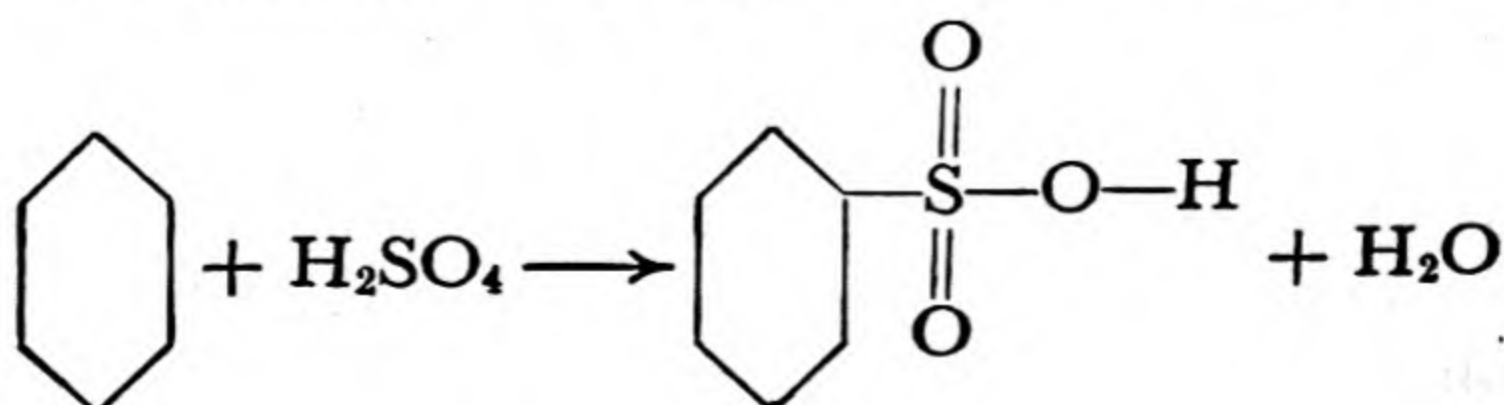
The sulfonic acid may be separated from the excess of sulfuric acid by neutralization with lime, followed by filtration. The calcium salt of the sulfonic acid is soluble. The sodium salt is formed by the reaction of the calcium salt with sodium carbonate. Sulfonic acids are useful as intermediates in the synthesis of many organic compounds.

Hydroxide Derivatives. There are a number of compounds that contain the hydroxide group in place of an atom of hydrogen in the nucleus of the molecule of an aromatic hydrocarbon. The simplest of these compounds is *phenol*, C_6H_5OH, also known as *carbolic acid*. Similar compounds of toluene are the three *cresols*, isomeric compounds, in which the three hydroxide groups are in the ortho, meta, and para position to the methyl group. These substances are weakly acidic and are analogous to the hydroxycompounds of the nonmetallic elements.

Phenol is a product of the destructive distillation of coal and is also produced from benzene. The fusion of the sodium salt of benzene sulfonic acid with sodium hydroxide produces the sodium salt of phenol, called sodium phenoxide or phenolate, and sodium sulfite. Phenol may be prepared from this salt by reaction with sulfuric acid.

$$\text{C}_6\text{H}_5\text{SO}_2\text{OH} + 3\,\text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{ONa} + \text{Na}_2\text{SO}_3 + 2\,\text{H}_2\text{O}$$

$$2\,\text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{SO}_4 \longrightarrow 2\,\text{C}_6\text{H}_5\text{OH} + \text{Na}_2\text{SO}_4$$
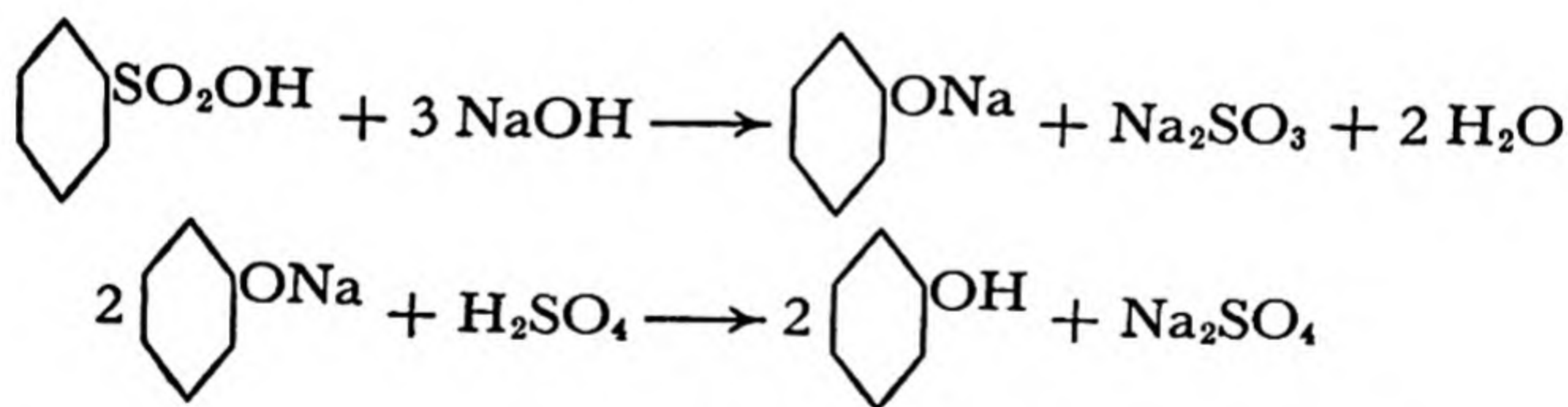
Phenol is also produced from benzene by forming chlorobenzene, which is then heated with sodium hydroxide to form sodium phenoxide.

$$C_6H_5Cl + 2\,NaOH \longrightarrow C_6H_5ONa + NaCl + H_2O$$
$$C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl$$
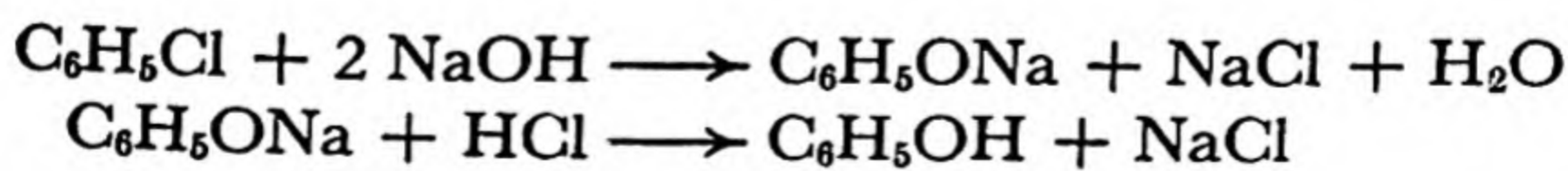
Phenol is a colorless solid that melts at 41°. It is a corrosive poison used in dilute solutions as a germicide. Trinitrophenol is the important military explosive, picric acid. Large quantities of phenol are used in the production of synthetic resins, such as Bakelite,

and in the synthesis of some of the dyes and other commercial products.

Nitro Compounds. Nitro compounds are prepared by the reaction of a mixture of concentrated nitric and sulfuric acids with aromatic hydrocarbons and with certain derivatives of these hydrocarbons. The reaction is called *nitration*. Sulfuric acid is a dehydrating agent in this reaction. In the course of the reaction, one, two, or three nitro groups may become substituted for atoms of hydrogen attached to the benzene nucleus.

$$\bigcirc + HNO_3 + H_2SO_4 \longrightarrow \overset{O=N=O}{\bigcirc} + H_2SO_4(H_2O)$$
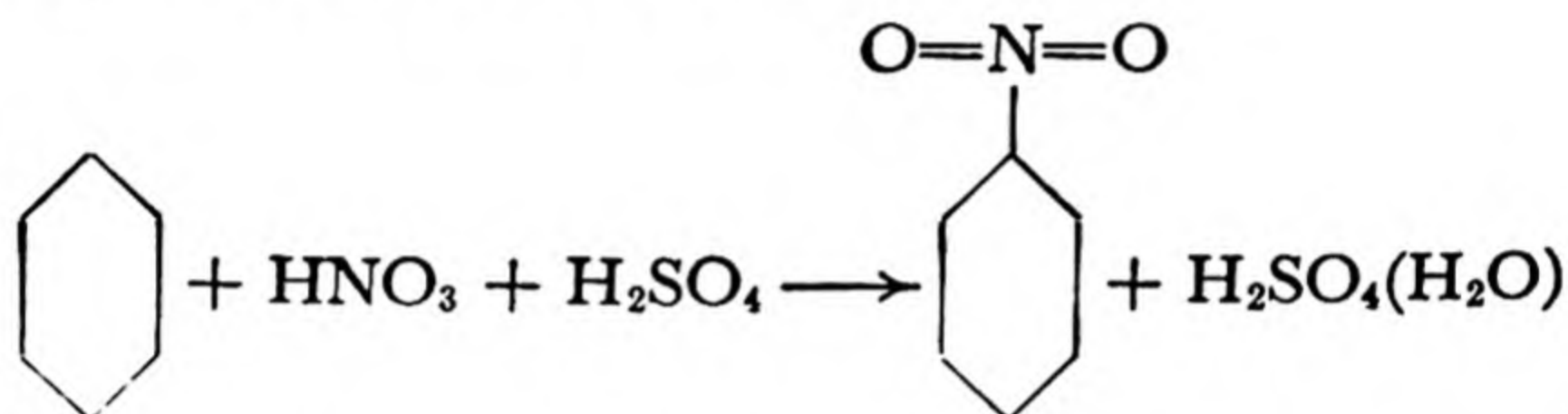
The number of nitro groups entering into the molecule depends on the temperature and concentration of the acids. The second nitro group enters the meta position. Three of the important military explosives are polynitro compounds.

T.N.T.   Picric Acid   Tetryl
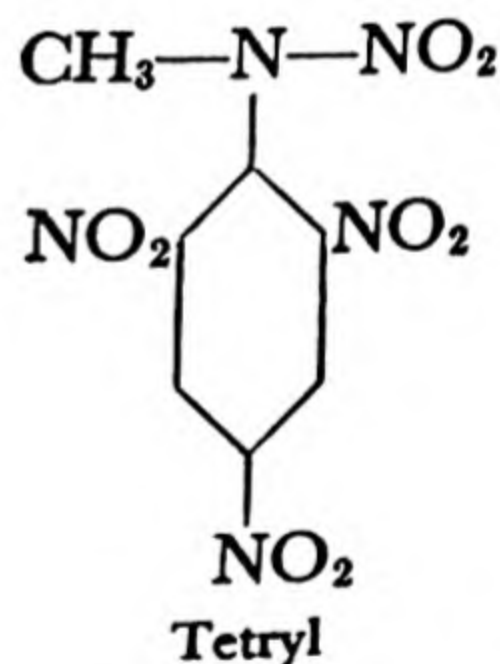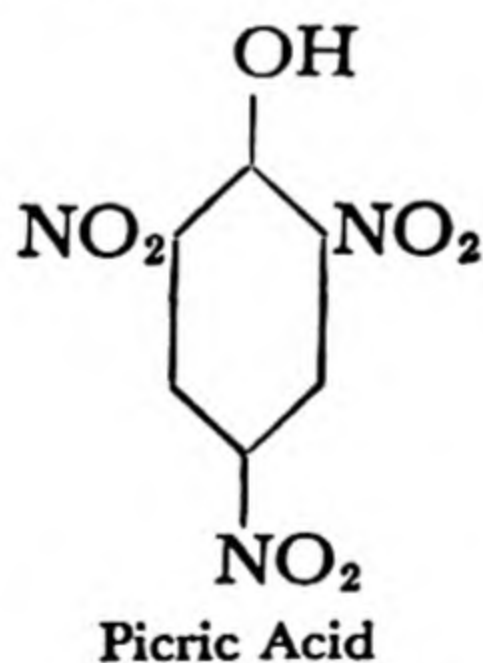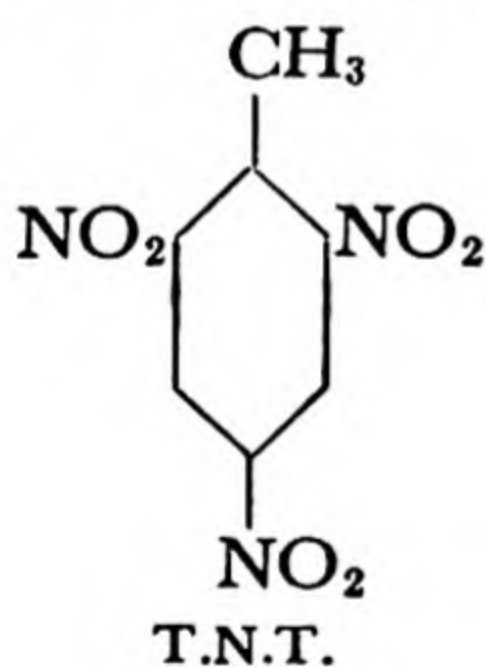
Aromatic Amines. The reduction of nitro compounds produces amines. *Aniline*, $C_6H_5NH_2$, is prepared industrially by the reduction of nitrobenzene with iron and water.

$$\overset{NO_2}{\bigcirc} + 2\,Fe + 4\,H_2O \longrightarrow \overset{NH_2}{\bigcirc} + 2\,Fe(OH)_3$$
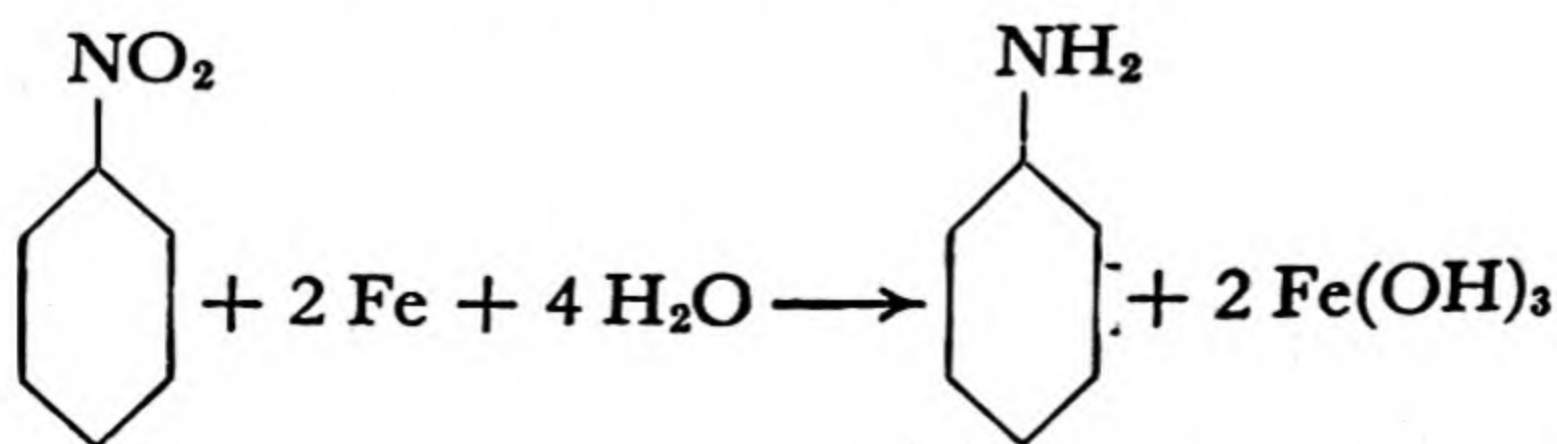
Aniline is also prepared by the reaction of benzyl chloride with

ammonia, using cuprous oxide to prevent the reverse reaction caused by the accumulation of ammonium chloride.

$$2\ C_6H_5Cl + 2\ NH_3 + Cu_2O \longrightarrow 2\ C_6H_5NH_2 + 2\ CuCl + H_2O$$
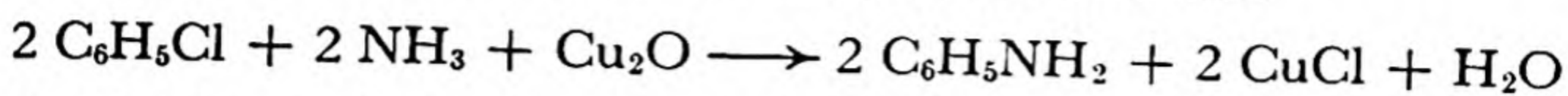
Aniline is a colorless liquid which boils at 184°. It is used so extensively in the preparation of dyes that these synthetic products are often called aniline dyes, although the preparation of many of them does not involve the use of aniline.

Amino Acids. These substances contain both the amino group, —NH₂, and the carboxyl group, —COOH. Consequently they are amphoteric substances. In addition to the properties of amines and of acids, they exhibit some special properties caused by the presence of both of these groups in the same molecule. If the amino group is attached to the carbon next to the carboxyl group, the product is an α-amino acid. The preparation of an α-amino acid from the corresponding simple acid may be brought about by chlorination to form the α-chloroacid, followed by reaction with ammonia. The reaction of acetic acid with chlorine in sunlight produces chloroacetic acid.

$$CH_3COOH + Cl_2 \longrightarrow CH_2ClCOOH + HCl$$
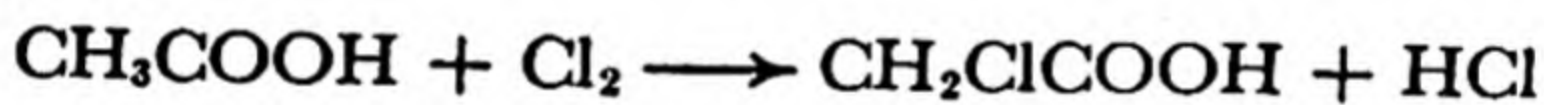
This compound reacts with ammonia to form glycine, aminoacetic acid.

$$CH_2ClCOOH + 2\ NH_3 \longrightarrow CH_2NH_2COOH + NH_4Cl$$
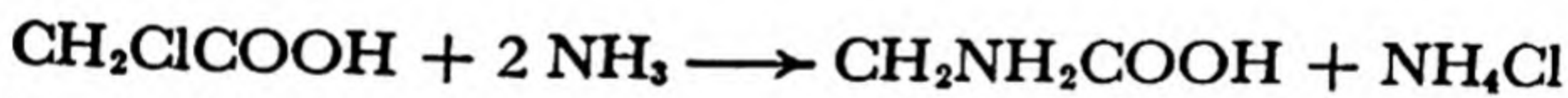
The proteins are complex organic materials which yield a mixture of α-amino acids by hydrolysis. Twenty-four different amino acids have been found among the hydrolysis products of a variety of proteins. Some of the natural amino acids, like glycine, are derivatives of aliphatic hydrocarbons, while others, like phenylalanine, contain aryl groups.

Glycine

Phenylalanine
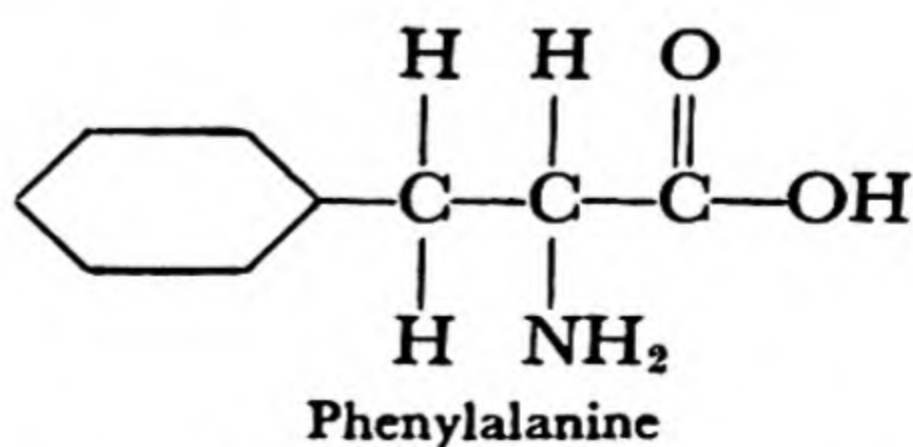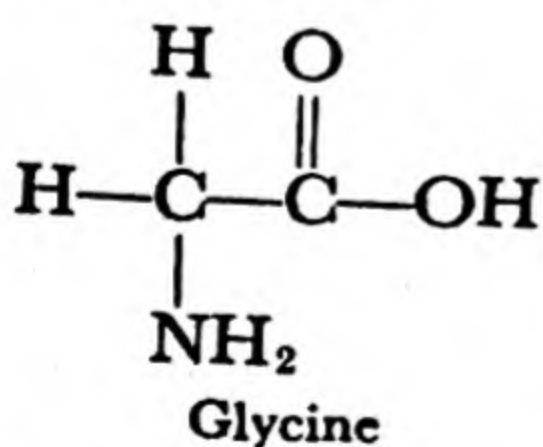
Only nine of these amino acids are required to support the growth of young animals. From these, the animal may build up the proteins

containing other amino acid units characteristic of the particular animal.

Synthetic Resins. The most familiar synthetic resin is *Bakelite*, a formaldehyde-phenol resin prepared by heating the substances together, with sodium hydroxide as a catalyst. When this product is heated under pressure in a mold, it hardens in the shape of the mold. The product is insoluble and infusible and is inactive chemically. It also has good electrical resistance. A number of objects are manufactured from formaldehyde-phenol resins, *e.g.*, pens, combs, phonograph records, and parts of electrical equipment such as sockets, switch-blocks, telephone receivers and transmitters, and many other articles. The composition of Bakelite resins may be modified by the use of other aldehydes and homologues of phenol in the mixture.

The most important of the acrylate resins are *Lucite* and *Plexiglas*, prepared by the polymerization of methyl methacrylate. The ester is prepared from acetone by the reactions indicated below:

$$CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow{HCN} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CN \xrightarrow[H_2SO_4]{CH_3OH} CH_2=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{||}}{C}-O-CH_3$$

Acetone   Methyl Methacrylate
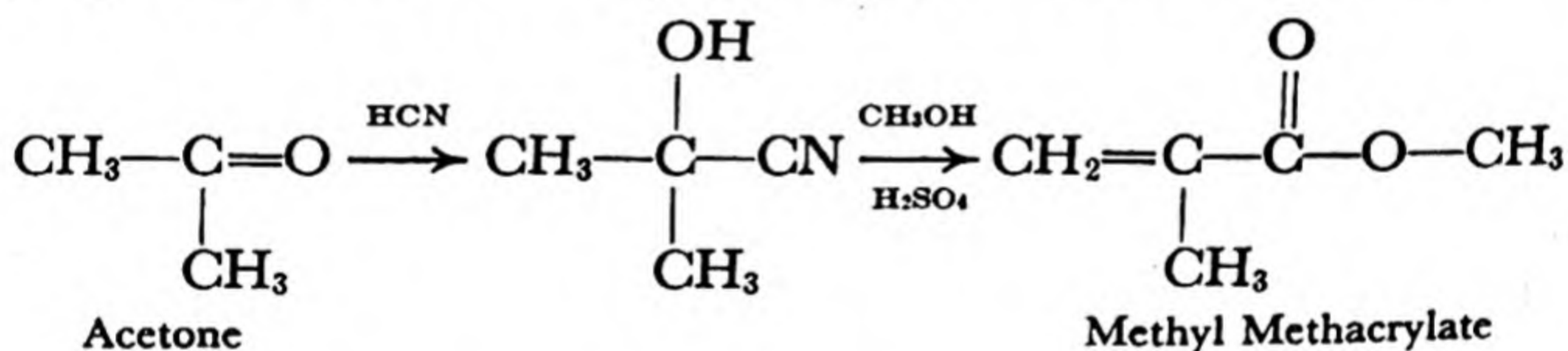
This substance polymerizes under the action of heat, ultraviolet light, and under the action of organic peroxides to produce a tough, transparent, light product, used for windows of airplanes. It is easily molded, and is used for lenses and many other articles. It has the unusual property of conducting light along a curved path, so that a light held at one end of a curved rod of this resin emerges at the other end.

Another series of resins is made from acetylene through the intermediate formation of vinyl chloride, $CH_2=CHCl$, or vinyl acetate, $CH_3COOCH=CH_2$. Vinyl chloride polymerizes to form a product that may be plasticized with tricresyl phosphate to form a resin sold under the trade name *Koroseal*. This resin is used in the manufacture of transparent belts, suspenders, watch bands, etc. It is also used in the waterproofing of fabrics. *Vinal* resins are produced by hydrolyzing the acetate to form polyvinyl alcohol.

This material condenses with aldehydes. Among the uses of this resin is the production of safety glass. (See page 394.)

Nylon is a polyamide formed by the reaction of the dicarboxylic acid, adipic acid, $HOOC(CH_2)_4COOH$, with hexamethylene-diamine, $H_2N(CH_2)_6NH_2$. Condensation occurs through the carboxyl groups of the acid and the amino groups of the diamine to give an end to end linkage and form long molecules. The molten product may be extruded to form fine filaments, spun to make thread. Bristles are made by extruding strands of suitable diameter.

Explosives. In addition to gunpowder and ammonium nitrate, the substances most extensively used as explosives are organic compounds containing nitrogen and oxygen. These compounds possess in common a certain degree of instability due to the fact that they are endothermal compounds. When decomposed they form gaseous products, and a large amount of heat is evolved. Consequently, the gaseous products are heated to a high temperature and occupy a large volume compared to that of the original substance. A substance that exhibits too great instability is not a useful explosive, for its decomposition cannot be controlled so as to have the explosion occur at the desired place. The common high explosives are of two types: *esters of nitric acid*, in which several nitrate radicals are present in one molecule of the compound, and *nitro compounds*.

Glyceryl nitrate, nitroglycerine, is an important high explosive. The pure substance decomposes with great violence, yielding the oxides of carbon and hydrogen and elementary nitrogen and oxygen.

$$4 C_3H_5(NO_3)_3 \longrightarrow 12 CO_2 + 10 H_2O + 6 N_2 + O_2$$
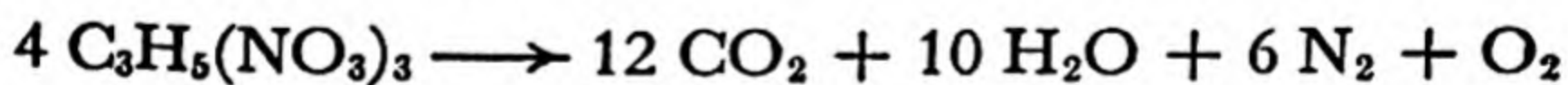
The instability of this substance is so great that a considerable amount of danger is involved in transporting and handling it. In 1867, Nobel discovered that nitroglycerine may be absorbed in finely divided porous earth, diatomaceous earth, to produce a powerful explosive that may be handled safely. This material, known as *dynamite*, is now commonly made by absorbing nitroglycerine in wood pulp or sawdust, with the addition of sodium nitrate or potassium nitrate. A special dynamite contains ammonium nitrate. Blasting gelatine, also discovered by Nobel, is composed of nitroglycerine gelatinized with 7–8 per cent of collo-

dion cotton containing about 12.1 per cent of combined nitrogen. This product is the most powerful of the industrial explosives.

Guncotton, cellulose trinitrate, is composed of white fibers having a nitrogen content of 13.2–13.5 per cent. In the fiber form it is a high explosive, but the gelatinized material is a low-order explosive suitable for use as a propellant. Guncotton is converted into a gelatinous mass by treatment with ether and alcohol. This material is shaped into particles of suitable size and dried. It is a *smokeless powder*, extensively used in the form of perforated cylindrical particles, varying in size, for guns of different calibers. *Cordite* is a gelatinized mixture containing 65 per cent of guncotton and 30 per cent of glyceryl trinitrate, stabilized by about 5 per cent of vaseline, shaped into cords and dried. This material contains the two explosive substances in a form which may be used as a propellant. Individually, each of these substances detonates with such violence that the shattering effect prevents its use as a propellant. *Mercuric fulminate*, $Hg(ONC)_2$, is used in priming caps for firing the propellant. The fulminate may be handled while moist, but detonates from friction and from impact when dry.

Nitro explosives are extensively used in shells for military purposes. Trinitrotoluene, T.N.T., $C_6H_2(CH_3)(NO_2)_3$, and picric acid trinitrophenol, $C_6H_2(OH)(NO_2)_3$, are both used in high explosive shells. These substances are sufficiently insensitive to shock to permit their use in shells fired from guns. The more sensitive guncotton and nitroglycerine are not suitable for such use. Trinitrotoluene mixed with ammonium nitrate gives the high explosive *amatol*, which is used in shells. For the detonation of high explosives, mercury fulminate is reinforced by a fairly sensitive, powerful, high explosive, such as Tetryl.

Dyes. Formerly, the dyestuffs were obtained entirely from natural products, *e.g.*, alizarin from madder root, and indigo from the indigo plant. Large amounts of the natural material were required to furnish small amounts of the dye, and the cost was great. In 1856, Perkin, a young British student, while attempting to synthesize the drug quinine, discovered a dye, mauve. Since that time a great number of dyes have been prepared by synthetic processes. The advantage of these synthetic products over the natural extracts is that they can be prepared in pure condition,

in larger quantities, and more economically. The color of the dye depends on the manner in which the atoms of the constituent elements are linked together. Certain molecular configurations always yield colored products, while different substituent groups modify the color, thus producing different shades of the same color. By-products of the destructive distillation of coal, separated from coal tar, are the crude materials used in the synthesis of many dyes, so that they are called *coal tar dyes*.

Drugs. Great progress has been made in the synthesis of known drugs and in the production of new drugs. The problem of separating and purifying the active principle in a drug is complex. The physiological action of a drug is often the result of several substances in the natural product. However, the active material of many drugs has been isolated and the composition and constitution have been determined. Once this was done, methods for the synthesis of the products have been developed. Some progress has been made in determining the particular grouping of atoms responsible for the physiological action of the drug. When this is known, it is often possible to prepare new drugs with greater beneficial effects than any previously known drugs, without the harmful effects that accompany the use of many natural preparations. *Procaine*, novocaine, for example, the familiar local anaesthetic is now largely used instead of cocaine.

Many substances, not known to occur among natural materials, have been synthesized and found useful as drugs. Aspirin, a product of this type, is now produced in large quantities by the reaction of acetic anhydride with salicylic acid. Methyl salicylate, a natural product, is also synthesized from salicylic acid.
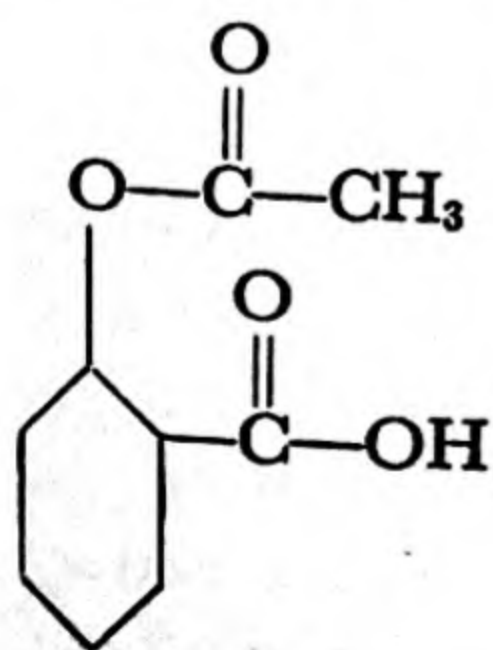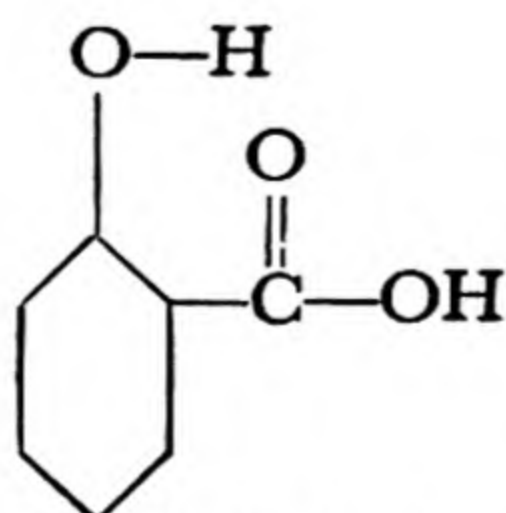
Aspirin   Salicylic Acid   Methyl Salicylate
(Oil of Wintergreen)
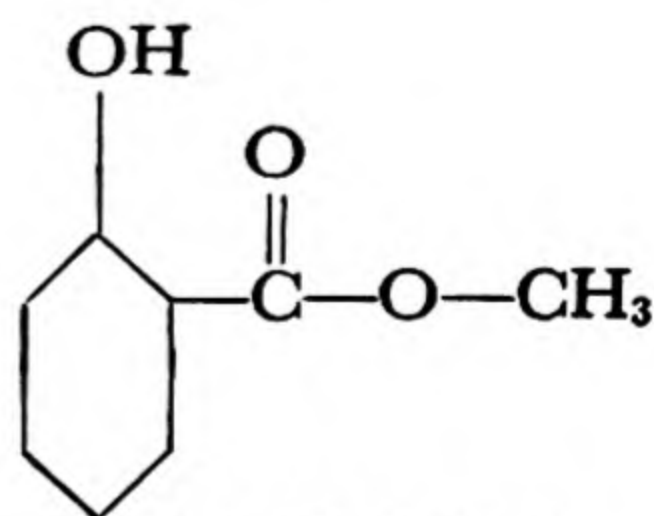
Much research has been done in the attempt to develop synthetic drugs that are poisonous to disease organisms but harmless to mankind. Ehrlich developed two synthetic drugs, salvarsan and neosalvarsan, which have been found effective in the treatment of syphilis. Other drugs have been developed for the treatment of sleeping sickness, amebic dysentery, and other diseases caused by protozoa. This type of treatment is known as *chemotherapy.*

Within recent years, the synthesis of the sulfa drugs provided materials for the treatment of bacterial infections caused by streptococci, pneumococci, and staphylococci. The first substance used successfully for the control of certain coccal infections was prontosil, a red dye. It was determined that only a portion of the molecule of this compound is effective for this purpose, and the synthesis of sulfanilamide followed. This substance is used in preference to prontosil. Other sulfa drugs which have specific advantages are now produced. The structural formulas of sulfanilamide and sulfapyridine are, respectively:
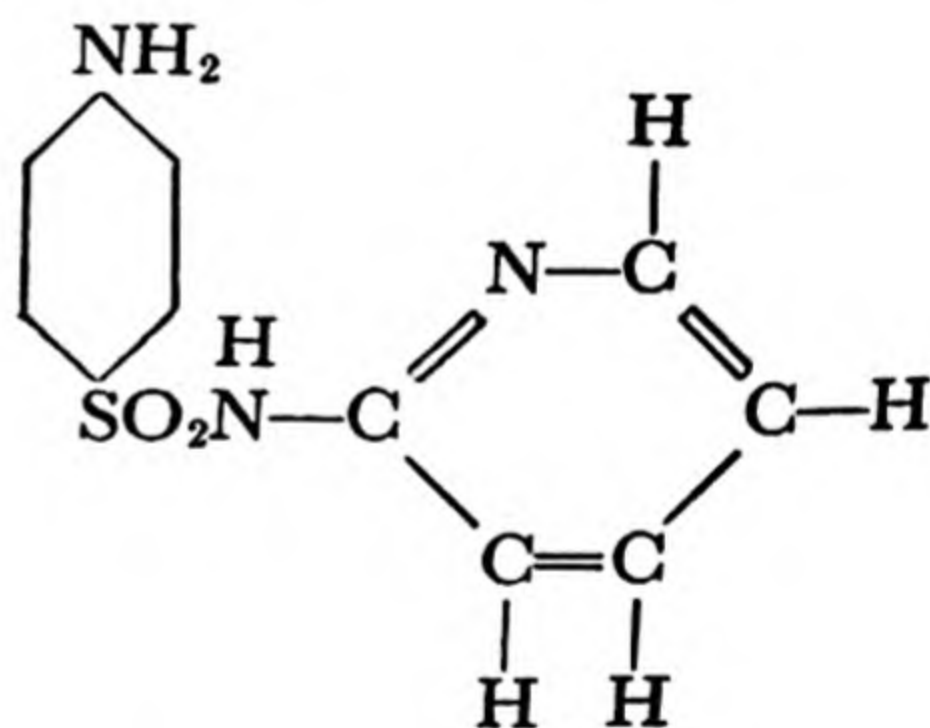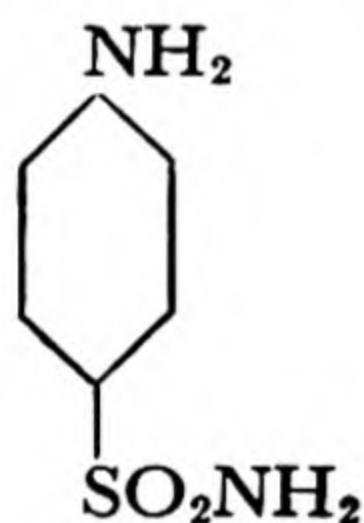
Sulfathiazole, sulfadiazine, and sulfaquanidine are additional sulfa drugs, which differ from sulfapyridine in the group substituted for one of the hydrogen atoms in the sulfonamide.

Hormones. The hormones are substances secreted by the ductless glands and transferred by the blood or lymph to other organs of the body. The glands producing these secretions are known as endocrine glands. Different hormones have different physiological action, and small quantities are usually sufficient to meet the requirements. *Adrenaline,* formerly obtained solely as an extract from the suprarenal gland of sheep, is now produced by synthetic processes. It is usually administered in dilute solution by sub-

cutaneous injection. *Thyroxine* is a product of the hydrolysis of the hormone thyroglobulin, which is produced in the thyroid gland. This hormone is a protein with activity which is due to thyroxine, an amino acid it contains. There is a large percentage of iodine in thyroxine, and disorders of the thyroid gland occur unless a sufficient supply of iodine is obtained from water or food. Extracts prepared from the thyroid glands of slaughtered animals and synthetic thyroxine are used in the treatment of such disorders. *Insulin*, a hormone secreted by ductless glands in the pancreas, is required for the proper oxidation of carbohydrates in the body. The absence of this hormone causes diabetes, recognized by the presence of glucose in the urine. Insulin, prepared from the pancreatic glands of animals, is injected to control this disease.

Foods. The most general and important use of organic compounds is as food. The animal body requires food to replace materials consumed in metabolic processes. There are three main classes of foods, *viz.*, the carbohydrates, fats, and proteins. Mineral salts and water are also required. With the exception of mineral salts and glucose, the foods do not pass directly and unaltered through the lining of the digestive tract to be absorbed in the circulatory system. Under the action of various enzymes in the digestive juices, the different classes of foods are hydrolyzed during digestion to form simpler molecules that may be assimilated. The carbohydrates, such as starch and the higher sugars, are converted into hexoses, the fats into glycerol and fatty acids, and the proteins into amino acids. The absorption of food occurs primarily in the small intestine. Absorbed hexoses are carried to the liver, where they are in part converted into glycogen, "animal starch," and stored until they are required to maintain the proper proportion in the blood. Glycerol and the fatty acids are absorbed and resynthesized into fats transported in the lymph. They are stored chiefly as tristearin, tripalmitin, and triolein in the abdominal cavity and in connective tissue. Proteins are absorbed as amino acids. Some of these pass into the general circulation and are used in building up tissue protein. The excess of the protein is largely converted into urea, carbon dioxide, and water. In the normal adult, the nitrogen intake in the form of proteins is equal to the nitrogen output in urea and other nitrogenous substances. The oxidation of food products

furnishes heat to maintain the body temperature and the energy for work.

Different vitamins are required for the proper functioning of the various organs of the body. Normally, an adequate supply of these may be obtained from food in a varied diet. When necessary, the supply of vitamins may be supplemented through the use of materials containing high concentrations of these substances, obtained from natural sources. Several of the vitamins are now available in the pure form produced by synthetic processes. The better the nature of the complex chemical processes occurring in the body is understood, the more intelligently may derangements in the normal functioning be treated.

EXERCISES

1. What is meant by a functional group?
2. For each of the following classes of derivatives, select one compound, write its structural formula, discuss the sources, and mention a use that indicates its economic value: (*a*) alcohols; (*b*) aldehydes; (*c*) ketones; (*d*) ethers; (*e*) acids; (*f*) amides; (*g*) esters.
3. How does esterification differ from neutralization?
4. What is a fat? an oil? What is the difference between edible oils, fuel oils, and lubricating oils?
5. Discuss the production of soap and some of the modifications in composition for special purposes. What are hard water soaps?
6. What are carbohydrates? Mention three important classes of carbohydrates and the uses of a member of each class.
7. What is meant by side-chain derivatives of aromatic hydrocarbons?
8. What three reactions may be used for the introduction of substituent groups into the aromatic hydrocarbons? Illustrate each by an equation.
9. Discuss the synthetic resins and the methods for preparing different types of resins and indicate some important uses.
10. What is the nature of an explosive? Into what classes may explosives be divided? Give examples of each type.
11. What is meant by chemotherapy? Illustrate by suitable examples.
12. What are the important classes of foods? What are the essential changes involved in the digestion and assimilation of each of these classes of foods?

SUPPLEMENTARY READINGS

Fuson, R. C., and H. R. Snyder, *Organic Chemistry,* John Wiley & Sons, Inc., New York, 1942.

Conant, J. B., *The Chemistry of Organic Compounds,* The Macmillan Company, New York, 1939.

Riegel, E. R., *Industrial Chemistry*, Reinhold Publishing Corporation, New York, 1937, chaps. 22, 33.

Hardy, R. E., "Producing Smokeless Powder by 1942 Methods," *Chem. Met. Eng.* **49,** 4, 76 (1942).

Bolton, E. K., "Development of Nylon," *Ind. Eng. Chem.* **34,** 53 (1942).

Major, R. T., "Industrial Development of Synthetic Vitamins," *Chem. Eng. News* **20,** 517 (1942).

Northey, E. H., "Chemical Side of Chemotherapy," *Ind. Eng. Chem.* **35,** 829 (1943).

PROBLEMS

I. GRAM EQUIVALENT WEIGHTS

1. It is found by experiment that 2.5 g. of calcium combine with 1 g. of oxygen. Calculate the weight of calcium that combines with 2 g. of oxygen; with 5 g. of oxygen; with 10 g. of oxygen; with 8 g. of oxygen. The quantity that combines with 8 g. of oxygen is the gram equivalent weight.

2. Silver oxide contains 93.097 per cent of silver. Calculate the gram equivalent weight of silver.

3. Calculate the gram equivalent weight of each element from the percentage of that element in the oxide shown in the following list:
   - (a) Calcium oxide   71.43% of calcium
   - (b) Carbon dioxide   27.27% of carbon
   - (c) Sulfur dioxide   50.00% of sulfur
   - (d) Zinc oxide   80.34% of zinc
   - (e) Phosphorus pentoxide   43.68% of phosphorus

4. From the weight ratios given in the following examples, calculate the gram equivalent weight of the elements in combination with oxygen.
   - (a) Mercurous oxide   50.1 g. of mercury, 2 g. of oxygen
   - (b) Boric oxide   1 g. of boron, 2.2 g. of oxygen
   - (c) Titanium dioxide   5 g. of titanium, 3.3 g. of oxygen
   - (d) Chromium trioxide   2.6 g. of chromium, 2.4 g. of oxygen
   - (e) Manganese dioxide   5.5 g. of manganese, 3.2 g. of oxygen

5. The gram equivalent weight of silver is 107.88 g. and of chlorine 35.46 g. Calculate the per cent of silver in silver chloride.

6. A 1 g. sample of magnesium chloride contains 0.2553 g. of magnesium. The equivalent weight of magnesium is 12.16. Calculate the gram equivalent weight of chlorine.

7. It is found by experiment that 2.5 g. of an oxide of iron contain 1.7484 g. of iron. What is the gram equivalent weight of iron in this oxide?

8. Magnesium oxide contains 60.32 per cent of magnesium and the bromide contains 13.20 per cent. Calculate the gram equivalent weight of bromine.

9. The quantities of each of the elements listed below hold 5.04 g. of hydrogen in combination:

Oxygen 40.00 g.   Chlorine 177.30 g.
Carbon 15.005 g.   Nitrogen 23.40 g.
Sulfur 80.15 g.   Phosphorus 51.70 g.

Calculate the gram equivalent weight of each element.

10. The combustion of 10 g. of mercuric sulfide yields 8.62 g. of mercury. This quantity of mercury combines with chlorine to form 11.66 g. of mercuric chloride. The equivalent weight or chlorine is 35.46. Calculate the gram equivalent weight of sulfur.

11. If 3.387 g. of a metal displace 0.378 g. of hydrogen, what is the gram equivalent weight of the metal?

12. When a strip of iron is suspended in a solution of copper sulfate, it is found that the loss of weight of the iron is 3.15 g. and that 3.586 g. of copper are displaced. The equivalent weight of iron is 27.92. Calculate the gram equivalent weight of copper.

13. A solution contains 1.8962 g. of stannous chloride. All of the tin in this solution is displaced by zinc and is found to weigh 1.187 g. The weight of zinc going into solution is 0.6537 g. The equivalent weight of zinc is 32.68. Calculate the gram equivalent weight of tin and of chlorine.

14. It is found that 1.773 g. of chlorine displace 3.996 g. of bromine from a bromide and that this same quantity of chlorine displaces 6.345 g. of iodine from an iodide, and 0.801 g. of sulfur from a sulfide. The equivalent weight of chlorine is 35.46. Calculate the gram equivalent weights of bromine, iodine, and sulfur.

15. It is found that 3.102 g. of phosphorus react with 10.638 g. of chlorine and that the chloride produced by this reaction will combine with an additional 7.092 g. of chlorine. Calculate the equivalent weight of phosphorus in each of these compounds. Reduce the ratio of the two equivalent weights of phosphorus to the simplest integral ratio.

II. FORMULAS

16. Calculate the number of gram atoms of oxygen in: (a) 32 g. of oxygen; (b) 48 g. of oxygen; (c) 50 g. of oxygen; (d) 6.4 g. of oxygen; (e) X g. of oxygen.

17. It is found that 1 gram atom of sulfur combines with 2 gram atoms of oxygen. Write the formula of this oxide. What is the ratio by weight in which the elements react to form this oxide? What is the gram equivalent weight of sulfur in this compound?

18. Derive the empirical formulas of the oxides having the composition shown in Problems 3 and 4.

19. A compound contains 30.75 per cent of potassium, 25.21 per cent of sulfur, and 44.04 per cent of oxygen. Derive the empirical formula representing this compound. What is the formula weight of the compound?

20. Two sulfates of iron have the composition shown by the following data: (a) iron, 27.93 per cent; sulfur, 24.05 per cent; oxygen, 48.02 per cent; and (b) iron, 36.76 per cent; sulfur, 21.11 per cent; oxygen 42.13 per cent. Derive the empirical formulas of these two sulfates, and calculate their molecular weights. If the valence of the sulfate radical is 2 −, what are the valences of iron in these compounds?

21. The percentage composition of a binary compound of carbon with hydrogen is: carbon, 92.25 per cent; hydrogen, 7.75 per cent. What is the empirical formula of the compound? If this were the true formula, what would the molecular weight be? Suppose that the molecular weight of the compound is found to be 78. What is the correct formula?

22. The gram equivalent weight of nitrogen in an oxide is 3.5. The mole of this oxide is 92 g. What is the formula of the oxide?

23. The composition of hydrated barium chloride is found to be: barium, 56.22 per cent; chlorine, 29.03 per cent; hydrogen, 1.64 per cent; oxygen, 13.10 per cent. Derive the empirical formula of the compound.

24. A 10 g. sample of hydrated sodium sulfate is found to contain 5.59 g. of water. The percentage composition of the salt is: sodium, 14.28 per cent; sulfur, 9.94 per cent; oxygen, 69.56 per cent; hydrogen, 6.21 per cent. Derive the empirical formula of (a) the hydrated salt and (b) the anhydrous salt.

25. Find the simplest formula corresponding to each of the following percentage analyses:

(a) Pb	64.11		C	29.71		H	6.18	
(b) Ti	38.76		F	61.24				
(c) Na	18.33		S	25.83		O	19.36	H₂O 36.28
(d) N	7.62		H	2.20		Sn	32.30	Cl 57.88
(e) H	0.77		S	62.06		O	37.17	
(f) H	2.22		C	26.67		O	71.11	
(g) Al	20.30		Cl	79.70				

Calculate the molecular weight of each compound according to the empirical formula.

26. The valences of a few simple and complex radicals are shown in the following lists:

(a) Na^{+1}, Mg^{+2}, Al^{+3}, NH_4^{+1}, Ca^{+2}, K^{+1}, H^{+1}, Fe^{+3}.

(b) Cl^{-1}, S^{-2}, Br^{-1}, $C_2H_3O_2^{-1}$, CO_3^{-2}, NO_3^{-1}, SO_4^{-2}, PO_4^{-3}.

Write the formulas for the compounds of each of the positive radicals with each of the negative radicals.

III. REACTING QUANTITIES OF SUBSTANCES

A. Reacting Weights

27. Calculate the number of moles of oxygen required for the complete combustion of (a) 1 gram atom of magnesium, (b) 5 gram atoms of carbon, (c) 10 gram atoms of sulfur, (d) 62 g. of phosphorus, (e) 0.1 mole of hydrogen.

28. What weight of potassium chlorate must be decomposed for the production of (a) 1 mole of oxygen, (b) 1 mole of potassium chloride, (c) 5 g. of oxygen, (d) 5 g. of potassium chloride.

29. Calculate the number of moles of sulfuric acid required for reaction with (a) 1 mole of aluminum oxide, (b) 10 g. of sodium hydroxide, (c) 2.46 g. of magnesium, (d) 14.8 g. of calcium hydroxide, (e) 0.796 g. of cupric oxide.

30. From the equation:

$$2 \, AlCl_3 + 3 \, MnO_2 + 6 \, H_2SO_4 \longrightarrow$$
$$Al_2(SO_4)_3 + 3 \, MnSO_4 + 3 \, Cl_2 + 6 \, H_2O$$
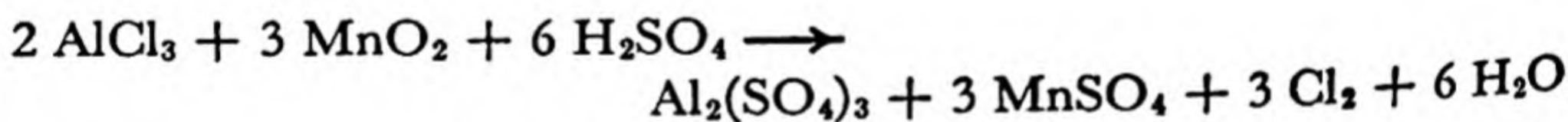
Calculate (a) number of moles of Cl_2 produced from 1 mole $AlCl_3$; from 5 moles; (b) number of moles of MnO_2 required to liberate 1 mole Cl_2.

From the equation:

$$3 \, Zn + 8 \, HNO_3 \longrightarrow 3 \, Zn(NO_3)_2 + 2 \, NO + 4 \, H_2O.$$
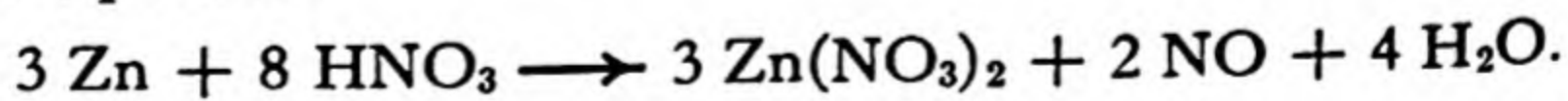
Calculate (a) number of moles of NO formed from 1 mole HNO_3; from 20 moles; (b) number of moles of Zn required to form 300 g. NO.

31. Calculate the weight of water and of copper, formed by the reaction of hydrogen with 10 g. of cupric oxide according to the equation:

$$CuO + O_2 \longrightarrow H_2O + Cu$$

32. What weight of calcium hydroxide is formed by the reaction of water with 2.8 g. of calcium oxide?

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
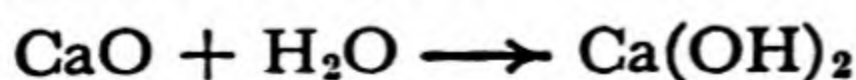
33. Calculate the weight of phosphoric acid produced by the reaction of 0.1 mole of phosphorus pentoxide with water.

$$P_2O_5 + H_2O \longrightarrow 2 HPO_3$$
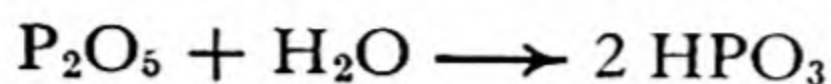
34. The equation representing the decomposition of potassium nitrate by heat is

$$2 KNO_3 \longrightarrow 2 KNO_2 + O_2$$
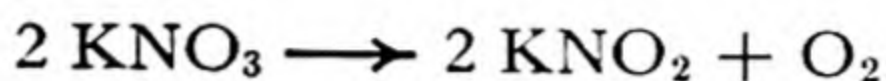
What weight of potassium nitrite would be formed from 21.3 g. of potassium nitrate?

35. What weight of slaked lime would be required to decompose completely 2 g. of ammonium chloride, and what would be the weight of each product formed?

$$2 NH_4Cl + Ca(OH)_2 \longrightarrow 2 NH_3 + CaCl_2 + 2 H_2O$$
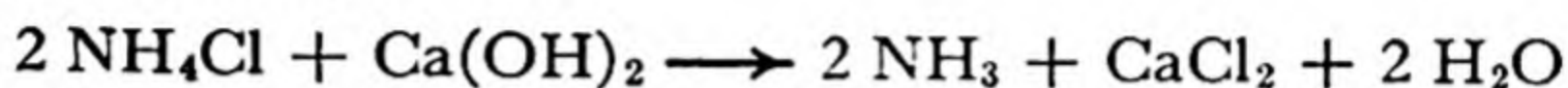
36. What weight of silver nitrate would be required for the complete decomposition of 7.48 g. of ferric chloride?

$$3 AgNO_3 + FeCl_3 \longrightarrow 3 AgCl \downarrow + Fe(NO_3)_3$$
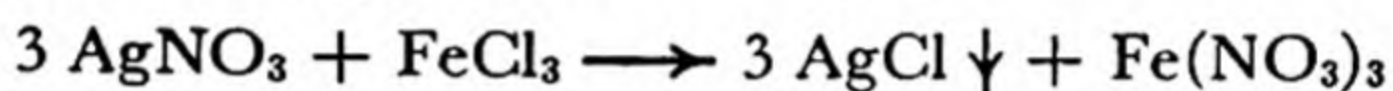
37. What weight of lead chromate would be precipitated by the reaction of lead acetate with 1.5 g. of potassium chromate?

$$Pb(C_2H_3O_2)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2 KC_2H_3O_2$$
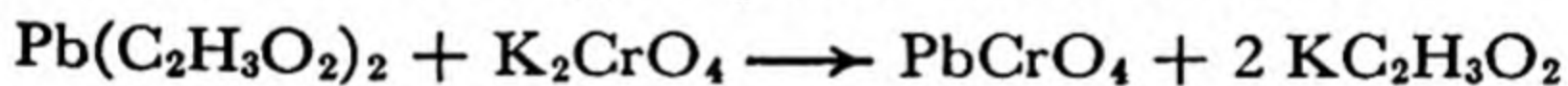
38. Find the weight of nitrogen formed by the complete decomposition of 10 g. of ammonium nitrite.

$$NH_4NO_2 \longrightarrow N_2 + 2 H_2O$$
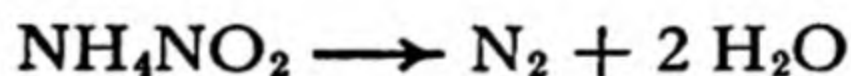
39. A series of reactions is carried out to produce the following products:

$$S \longrightarrow FeS \longrightarrow H_2S \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4 \longrightarrow Na_2SO_4$$
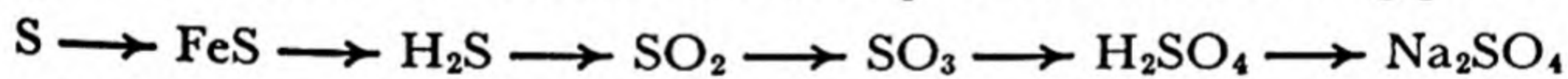
Calculate the weight of each product formed if $\frac{1}{5}$ gram atom of sulfur is used. Calculate the weight of each of the other materials required for these successive reactions.

40. What weight of concentrated sulfuric acid of specific gravity 1.8, containing 98 per cent of the acid, would be required for complete reaction with 10 g. of sodium chloride?

41. Concentrated hydrochloric acid has a specific gravity of 1.19 and contains 38 per cent of the acid. Calculate the weight of this solution required to prepare 1 liter of a solution containing 1 mole of hydrochloric acid.

42. If 10 g. of bromine react with a solution containing 10 g. of potassium hydroxide, what weight of each salt is produced and what weight of potassium hydroxide remains in solution?

$$Br_2 + 2 KOH \longrightarrow KBr + KBrO + H_2O$$

43. A 2 g. sample of sodium chloride is dissolved in water, and an excess of silver nitrate is added to the solution, producing a precipitate of silver chloride.

$$NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$$
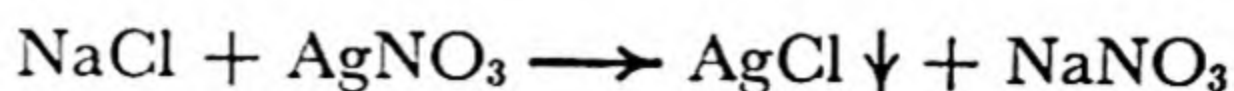
The precipitate is found to weigh 4.628 g. Assuming that all of the chloride in this precipitate is from sodium chloride, calculate the per cent of sodium chloride in the sample.

44. How many grams of phosphorus are required to produce 1 liter of phosphoric acid of specific gravity 1.61, containing 75 per cent of phosphoric acid, H_3PO_4?

45. Calculate the per cent of magnesium carbonate in a sample of magnesite if 1 g. yields 0.43 g. of carbon dioxide.

$$MgCO_3 + 2\ HCl \longrightarrow MgCl_2 + CO_2 + H_2O$$

46. What weight of barium sulfate could be obtained from a 1 g. sample of iron pyrite containing 35 per cent of sulfur?

47. How many pounds of aluminum may be obtained from a ton of bauxite ore that contains 65 per cent of aluminum oxide?

48. Sulfuric acid may be made by a process involving the following reactions:

$$4\ FeS_2 + 11\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ SO_2$$
$$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 + NO$$
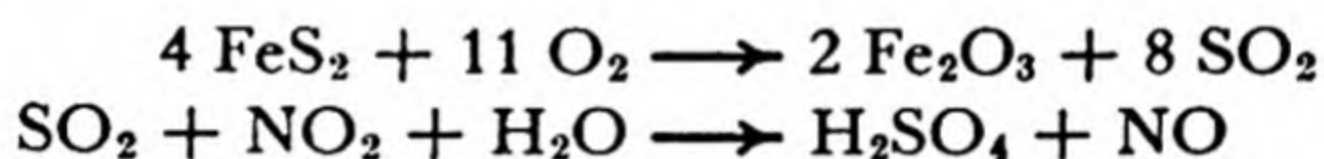
Calculate the weight of sulfuric acid formed from 600 g. of iron disulfide. What weight of 98 per cent sulfuric acid may be obtained? What would be the volume of this solution if its specific gravity were 1.8?

49. Calculate the weight of calcium hydroxide required to neutralize the hydrochloric acid in 100 ml. of a solution having a specific gravity of 1.19 and containing 38 per cent of the acid. What weight of calcium chloride would be formed?

B. Reacting Volumes of Gases

(In all problems in this section, assume that the gas volumes are measured under the same conditions of temperature and pressure.)

50. What volume of oxygen would be required for the complete combustion of 200 ml. of acetylene, and what would be the volume of carbon dioxide produced?

$$2\ C_2H_2 + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ H_2O$$
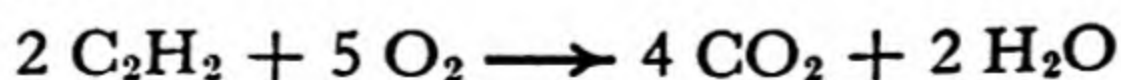
51. What volume of carbon dioxide would be formed by the combustion

of 4.48 liters of ethylene? Also, what would be the volume of water vapor formed?

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$
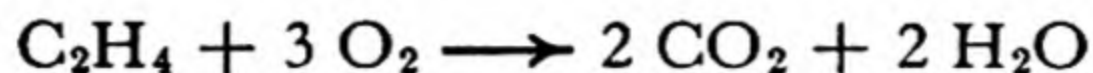
52. Calculate the volume of sulfur dioxide required to convert the sulfur in 20 ml. of hydrogen sulfide into free sulfur.

$$SO_2 + 2\,H_2S \longrightarrow 3\,S + 2\,H_2O$$
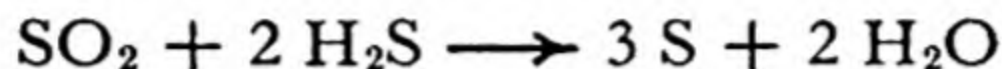
53. Calculate the volume of oxygen required for the complete combustion of 200 ml. of phosphine, PH_3.

$$2\,PH_3 + 4\,O_2 \longrightarrow P_2O_5 + 3\,H_2O$$
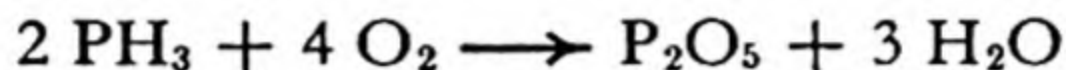
54. Calculate the volume of oxygen required to oxidize 10 liters of ammonia to nitric oxide and water.

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O$$

55. Calculate the volume of chlorine formed by the oxidation of 500 ml. of hydrogen chloride gas.

$$4\,HCl + O_2 \longrightarrow 2\,H_2O + 2\,Cl_2$$

What volume of oxygen would be required?

56. If 31.4 ml. of hydrogen were mixed with 112.7 ml. of oxygen and the mixture exploded, what volume of oxygen would be left?

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$
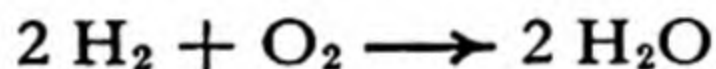
57. If 20 ml. of carbon monoxide were mixed with 15 ml. of oxygen and the mixture exploded, what volume of gases would remain?

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$
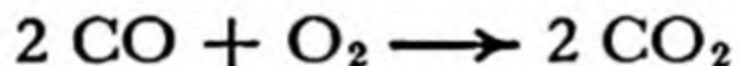
58. What volume of oxygen would be required for the complete combustion of 125 ml. of gaseous carbon disulfide? What volumes of carbon dioxide and sulfur dioxide would be formed?

$$CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2$$
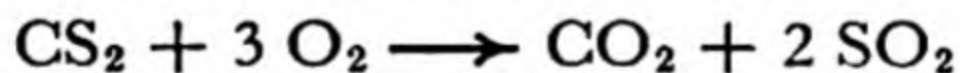
59. Assuming that the molecular per cent of oxygen in air is 20, calculate the volume of air required for the combustion of 100 ml. of hydrogen.

C. Reacting Weights and Volumes

(Assume that gases are measured under standard conditions of temperature and pressure unless otherwise specified.)

60. What volume of oxygen is produced by the decomposition of 10 g. of potassium chlorate?

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$
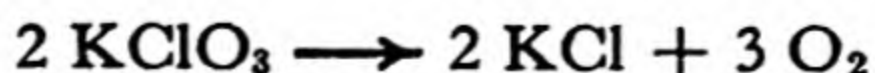
61. (a) What volume of hydrogen is obtained by the reaction of 1 g. of metallic magnesium with dilute hydrochloric acid? (b) What volume of hydrogen is obtained by the reaction of 1 g. of metallic magnesium with dilute sulfuric acid?

62. Calculate the volume of hydrogen sulfide produced by the reaction of an excess of hydrochloric acid with 0.2 mole of ferrous sulfide.

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S$$

63. Calculate the volume of methane, CH_4, evolved by heating 4.1 g. of sodium acetate with sodium hydroxide.

$$NaC_2H_3O_2 + NaOH \longrightarrow Na_2CO_3 + CH_4$$
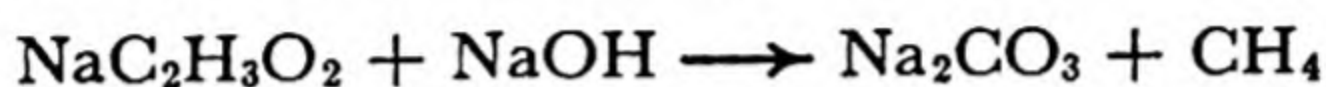
64. Calculate the weight of potassium hydroxide required to bring about the complete decomposition of 3.26 g. of ammonium sulfate. What would be the volume of ammonia evolved?

$$2\,KOH + (NH_4)_2SO_4 \longrightarrow K_2SO_4 + 2\,NH_3 + 2\,H_2O$$
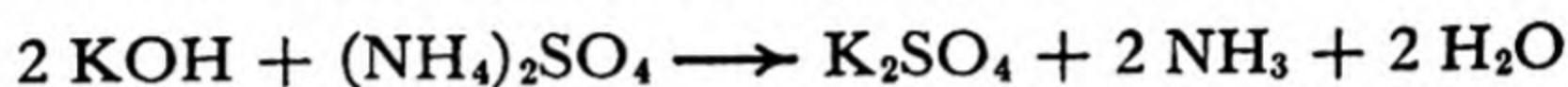
65. Calculate the volume of hydrogen sulfide obtained by the action of an excess of hydrochloric acid on 10 g. of stannous sulfide.

$$2\,HCl + SnS \longrightarrow SnCl_2 + H_2S \uparrow$$
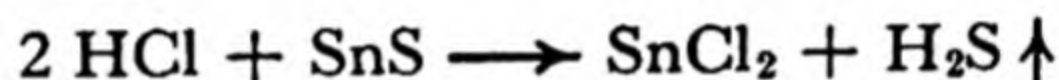
66. Calculate the volume of sulfur dioxide formed by the complete combustion of 4 g. of sulfur.

$$S + O_2 \longrightarrow SO_2$$
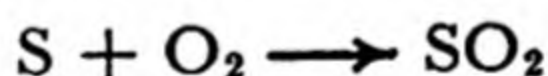
67. If 7.78 liters of carbon dioxide were dissolved in an excess of sodium hydroxide, what weight of sodium carbonate would be produced?

$$CO_2 + 2\,NaOH \longrightarrow Na_2CO_3 + H_2O$$
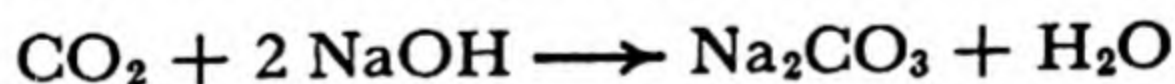
68. Into a solution of 10 g. of potassium hydroxide 1.9 liters of hydrogen bromide were passed. Calculate (a) the weight of potassium bromide formed, (b) the weight of potassium hydroxide neutralized, (c) the weight of the excess of potassium hydroxide left in solution.

$$HBr + KOH \longrightarrow KBr + H_2O$$

69. What weight of metallic iron would be required to produce 10 liters of hydrogen gas when acted on by hydrochloric acid?

$$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$$

70. In a potassium carbonate solution 56 liters of chlorine gas were absorbed. Calculate (a) the weight of potassium chloride formed, and (b) the volume of carbon dioxide liberated.

$$2\,Cl_2 + K_2CO_3 + H_2O \longrightarrow 2\,KCl + 2\,HOCl + CO_2$$
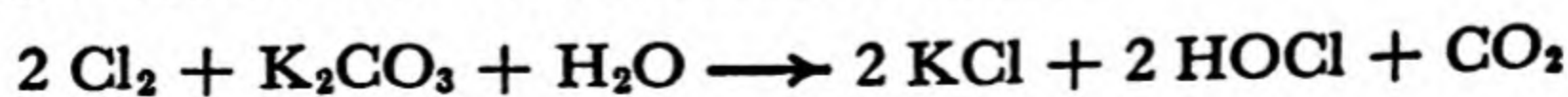
71. A sample of crude dolomite contained 54 per cent of calcium carbonate and 42 per cent of magnesium carbonate. Calculate the volume of carbon dioxide evolved when 5 g. of the sample are treated with hydrochloric acid.

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$
$$MgCO_3 + 2\ HCl \longrightarrow MgCl_2 + CO_2 + H_2O$$
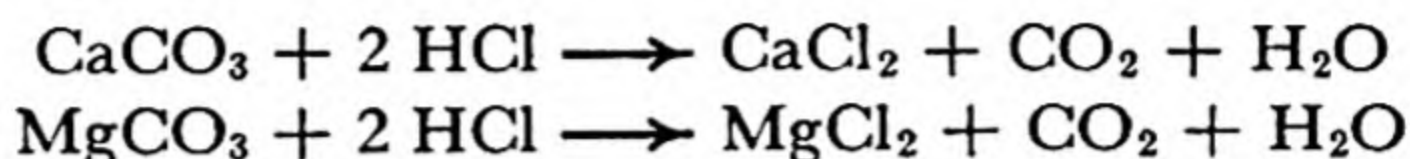
72. A sample of impure aluminum weighing 0.03 g. yields 35.43 ml. of hydrogen when it reacts with hydrochloric acid. Calculate the per cent of aluminum in the sample.

$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2$$
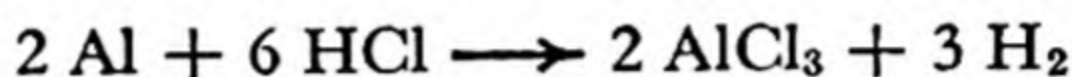
73. What volume of air — assumed to be composed of four volumes of nitrogen and one volume of oxygen — is necessary to burn the acetylene from 10 g. of calcium carbide?

$$CaC_2 + 2\ H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$
$$2\ C_2H_2 + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2$$
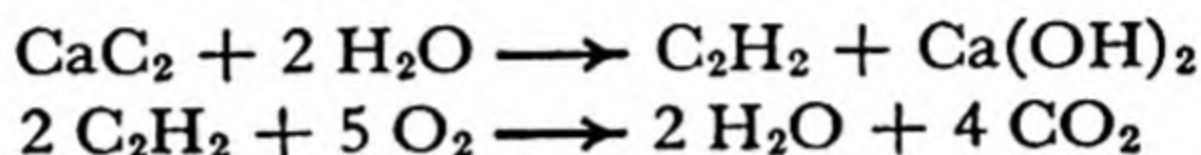
74. Two moles of sodium chloride are treated with concentrated sulfuric acid, and the hydrogen chloride evolved is oxidized by manganese dioxide. What volume of chlorine is produced?

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
$$4\ HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2\ H_2O$$

75. Assume that 11.17 g. of iron enter into the reactions indicated by the following equations:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$
$$6\ FeSO_4 + 3\ H_2SO_4 + 2\ HNO_3 \longrightarrow 3\ Fe_2(SO_4)_3 + 2\ NO + 4\ H_2O$$
$$Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 24\ H_2O \longrightarrow 2\ NH_4Fe(SO_4)_2(H_2O)_{12}$$
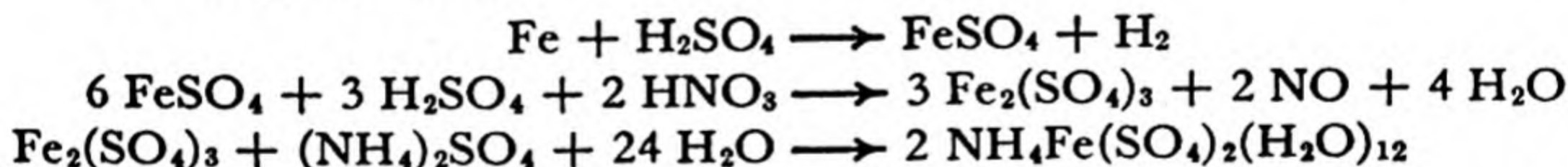
Calculate (a) the weight of $FeSO_4$ formed, (b) the volume of the hydrogen formed, (c) the weight of HNO_3 used, (d) the weight of the final product.

IV. THE GAS LAWS

76. Correct to standard conditions, the volumes of gases measured under the following conditions:

	Volume	Temperature	Pressure
(a)	25.1 ml.	15°	770 mm.
(b)	38.7 ml.	20°	750 mm.
(c)	36.0 ml.	0°	740 mm.
(d)	100.0 ml.	− 13°	750 mm.
(e)	75.0 ml.	17°	765 mm.

77. A quantity of oxygen is collected over water and found to occupy a volume of 32.2 ml. at 12° and 780 mm. Calculate the volume of the dry gas at standard conditions.

78. A gas sample occupies a volume of 100 ml. at 0° and 760 mm. Calculate its volume at 18° and 765 mm.

79. A certain quantity of a gaseous substance has a volume of 50 ml. under standard conditions. What would its volume be if it were collected over water at 20° and 755 mm.?

80. One liter of hydrogen and 4 liters of helium are pumped into a container having a volume of 2 liters. Calculate the total pressure and the partial pressure of each gas at 0°.

81. Calculate (a) the volume occupied by 5 moles of hydrogen chloride at 20° and 740 mm., (b) the volume occupied by 2 moles of carbon dioxide at 30° and 765 mm., (c) the volume occupied over water by 4 g. of oxygen at 23° and 755 mm., (d) the volume of the oxygen collected over water at 23° and 755 mm., produced by the heating of 12.25 g. of potassium chlorate.

82. Assume that a cylinder of liquid ammonia contains 17 kg. of the liquid.

    (a) How many liters of ammonia gas at standard conditions will this liquid yield?

    (b) Approximately how many liters of concentrated ammonia solution (28.3 per cent, density 0.9 g. per ml.) can be prepared?

    (c) What is the approximate normality of this solution?

    (d) How many liters of 3 N. sulfuric acid will be required to neutralize this solution? How many liters of 3 M. sulfuric acid?

    (e) In each case, what weight of salt will be formed in the neutralization?

    If this ammonia is "cracked" into its constituent gases, find:

    (f) The volume of the mixed gases at standard conditions.

    (g) The partial pressure of each constituent of the mixed gases.

    (h) If the volume of the original ammonia cylinder was 33.6 liters, find the pressure, in atmospheres, required to force the mixed gases back into the original cylinder.

    (i) If the ammonia is treated by the Ostwald process, with subsequent oxidation of the nitric oxide, what weight of nitrogen dioxide would be formed?

    (j) What weight of nitric acid could be formed by the absorption of this nitrogen dioxide gas in water in the absence of air?

V. CONCENTRATION OF SOLUTIONS

83. Calculate the gram equivalent weights of the following substances:

HCl, $Ca(OH)_2$, H_2SO_4, $Pb(NO_3)_2$, $AgNO_3$, H_3PO_4, $Al_2(SO_4)_3$.

84. How many moles of each of the following substances are required to prepare 500 ml. of a 1 molar solution: phosphoric acid, potassium hydroxide, magnesium sulfate? What is the normality of each of these solutions?

85. Calculate the molarity of the following solutions: (a) 1 mole of Na_2SO_4 in 500 ml. of solution; (b) 5 g. equivalent weights of KCl in 2 liters of solution; (c) 2 g. of $CaSO_4(H_2O)_2$ in 1000 ml. of solution; (d) 8 g. of NaOH in 250 ml. of solution; (e) 73 g. of HCl in 750 ml. of solution; (f) 5 g. of $Al_2(SO_4)_3$ in 432 ml. of solution; (g) 0.025 g. of Ag_2SO_4 in 1000 ml. of solution.

86. Concentrated sulfuric acid has a specific gravity of 1.8 at ordinary temperatures and contains 98 per cent of the acid. Calculate the molarity of the solution and the mole fraction of sulfuric acid.

87. A hydrochloric acid solution has a specific gravity of 1.19 at room temperature and contains 38 per cent of the acid. Calculate the normality of this solution. What volume of this solution would be required for the preparation of a liter of 1 N. HCl? 3 N. HCl? 0.3 N. HCl?

88. Concentrated nitric acid has a specific gravity of 1.42 at ordinary temperatures and contains 70 per cent of the acid. Calculate: (a) the normality, (b) the molarity, (c) the molality of the solution, and (d) the mole fraction of nitric acid in this solution.

89. Calculate the molal concentrations of the various solutes in the solutions listed in the following table.

	Weight of Solute	Weight of Water	Molal Concentration
$C_{12}H_{22}O_{11}$	17.1 g.	25 g.	
$C_6H_{12}O_6$	0.36	20	
C_2H_5OH	230.0	2500	
CON_2H_4	6.0	250	
C_3H_6O	23.2	100	
H_2O_2	170.0	500	

90. What volume of 0.5 N. sulfuric acid is required for the neutralization of a solution containing 10 g. of sodium hydroxide?

91. What volume of 0.2 M. hydrochloric acid is required for the complete decomposition of 5 g. of calcium carbonate?

92. If 25 ml. of a 0.38 N. acidic solution are equivalent to 30 ml. of a basic solution, what is the normality of the base?

93. If 21.2 g. of anhydrous sodium carbonate are treated with the minimum volume of acid required for complete reaction:

(a) What volume of half-molar sulfuric acid is required?

(b) What would be the normality of the sodium sulfate solution formed, assuming that the volume of solution after reaction is the same as that of the acid taken in (a)?

(c) If all the carbon dioxide is driven out, dried, and collected at 27° and 750 mm., what volume will it occupy?

94. Enough calcium oxide is used to convert 10.6 g. of sodium carbonate into calcium carbonate and sodium hydroxide, and the calcium carbonate is removed by filtration.

(a) To what volume must the resulting sodium hydroxide solution be diluted in order that a tenth-molar solution be prepared?

(b) It is found that 15 ml. of this tenth-molar sodium hydroxide solution are neutralized by the following: 30 ml. hydrochloric acid; 15 ml. sulfuric acid; 10 ml. phosphoric acid.

Calculate the normality and molarity of each of these acidic solutions.

VI. MOLECULAR AND ATOMIC WEIGHTS

95. The weight of a liter of oxygen under standard conditions of temperature and pressure is 1.429 g. Under similar conditions, the same volume of certain other gases weighs: (a) 1.17 g.; (b) 0.77 g.; (c) 1.78 g.; (d) 7.14 g.

Calculate the molecular weights of these gases by reference to oxygen.

96. If 34.2 ml. of a certain gas at 20° and 700 mm. weigh 0.0447 g., what is the molecular weight of the gas?

97. Calculate the molecular weight of chloroform from the following: 0.22 g. of the liquid vaporized in the Victor Meyer apparatus displaced 45 ml. air collected over water at 20° and 755 mm.

98. What is the molecular weight of a compound if 0.716 g. occupy 327.6 ml. in the gaseous state at 200° and 750 mm.?

99. If 0.091 g. of a gaseous substance occupy a volume of 33.5 ml. at 100° and 770 ml., what is the molecular weight of the substance?

100. If 0.15 g. of a substance yields 30.5 ml. of vapor at 95° and 400 mm., what is its molecular weight?

101. Calculate the density relative to air of chlorine, carbon dioxide, and ammonia.

102. Calculate the volume, under standard conditions, occupied by

(a) 4 g. of methane, (b) 7.3 g. of hydrogen chloride, (c) 9.2 g. of nitrogen dioxide, (d) 10 g. of sulfur dioxide.

103. Calculate the freezing point and boiling point of water from a solution which contains 100 g. of mannitol, $C_6H_{14}O_6$, in 1000 g. of water.

104. What weights of methanol, CH_3OH, glycerol, $C_3H_8O_3$, and ethylene glycol, $C_2H_6O_2$ (Prestone), respectively, must be added to a liter of water to lower the freezing point to approximately 0° F.?

105. Calculate the freezing point depression in each of the solutions mentioned in Problem 89.

106. Calculate the molal depression of the freezing point of the solvents from the data in the following table:

Substance Dissolved	Weight of Solute (g.)	Weight of Solvent (g.)	Observed Lowering of Freezing Point (° C.)	Molal Depression
$C_{12}H_{22}O_{11}$	171.00	250	3.72	
$C_{10}H_8$	12.80	200	2.56	
$C_{10}H_{16}O$	1.52	25	2.05	
C_6H_6	3.90	50	7.50	
$C_8H_{10}O_2$	25.50	125	7.80	
C_2H_5OH	13.80	100	35.40	

107. Calculate the molecular weights of the substances yielding the following experimental data:

(a) The freezing point of water is depressed 0.62° by 1.08 g. of solute in 100 g. of water.

(b) The freezing point of benzene is depressed 1.28° by 4.0 g. of a solute in 125 g. of benzene.

(c) The boiling point of benzene is raised 0.15° by 8 g. of a solute in 125 g. of benzene.

(d) The boiling point of water is raised 0.26° by 9 g. of a solute in 100 g. of water.

108. Three substances have the composition C 40.00 per cent, O 53.33 per cent, H 6.67 per cent. From the data below, find the true formulas:

(a) 250 ml. of A at 950 mm. and 91° weigh 0.312 g.

(b) 3 g. of B in 25 g. of water lower the freezing point 2.48°.

(c) 0.27 g. of C in 10 g. of water raises the boiling point 0.078°.

109. Two substances have the composition: nitrogen 30.43 per cent and oxygen 69.57 per cent. It is found, however, that under standard conditions 200 ml. of one weigh 0.41 g., and 125 ml. of the other weigh 0.512 g. Derive the true formula of each.

110. The smallest weight of the element X in 1 mole of any compound

of X is found by experiment to be 11.73 g. An oxide of this element contains 27.273 per cent of X. Calculate the atomic weight of X.

111. A metal yields an oxide in which 16 parts by weight of oxygen combine with 20.38 parts of the metal, and a chloride in which 35.46 parts of chlorine combine with 16.98 of the metal. What is the atomic weight of the metal?

112. An oxide of an element contains 23.95 per cent of oxygen, and a chloride contains 45.60 per cent of chlorine. Calculate the equivalent weight and the atomic weight of this element.

113. Calculate the approximate atomic weight of the element Y from the following data.

Compound of Y With	Weight of 1 Liter of Gaseous Compound (Standard Conditions) (g.)	Per Cent of Y in Compound
Oxygen	3.036	52.94
Chlorine	6.869	7.80
Sulfur	3.398	15.77
Oxygen	1.250	42.86
Hydrogen	1.250	85.72
Nitrogen	2.322	46.13

114. Calculate the exact atomic weight of the element X according to the following data.

Compound of X With	Molecular Weight of Compound	Per Cent of X in Compound
Iron	161.8	65.6
Copper	134.1	52.8
Mercury	235.2	15.1
Aluminum	132.5	79.8
Phosphorus	136.6	77.5
Phosphorus	207.7	85.1
Silicon	168.9	83.5
Tin	260.3	54.4
Carbon and hydrogen	84.7	83.5

2 g. of a compound of this element with hydrogen contain 1.9447 g. of X.

VII. PRODUCTS OF ELECTROLYSIS

115. If an electric current deposits 5.39 g. of silver, what weight of the following substances would be deposited by the same current: copper, mercury, lead, bismuth, chlorine, bromine, oxygen, hydrogen?

116. What weights of cadmium and iodine would be deposited from a solution of cadmium iodide by the passage of a 2-ampere current through the solution for 3 hours?

117. What volumes (S. T. P.) of hydrogen and oxygen would be liberated by the passage of a 2.5-ampere current through a solution of sodium sulfate for 30 minutes?

118. If a current deposits 10.78 g. of silver from a solution of a silver salt, what weight of copper from copper sulfate, of mercury from mercurous sulfate, and of cadmium from cadmium sulfate would be deposited by the same current? What volumes (S. T. P.) of hydrogen and of oxygen would be liberated from sulfuric acid solution by this current?

119. What weight of copper would be deposited from cupric chloride by 3214 coulombs of electricity? What weight and volume (S. T. P.) of chlorine?

120. How long must a 5.58-ampere current flow through a solution of sodium chloride in a Nelson cell in order to cause the formation of 5 moles of sodium hydroxide?

121. It is found that the same electric current passed through a series of cells deposits 10.78 g. of silver, 6.9666 g. of bismuth, 3.1785 g. of copper, 0.56 liter of oxygen, and 1.12 liters of chlorine. Calculate the equivalent weight of each of these elements.

122. What must be the amperage of a current in order to deposit 1.589 g. of copper in 1 hour and 20 minutes?

VIII. EQUILIBRIUM CONSTANTS

123. Calculate the apparent degree of ionization of the following solutes from the freezing point depression in aqueous solution:
    (a) 0.2 M. HCl, freezing point, $- 0.708°$.
    (b) 0.5 M. KCl, freezing point, $- 1.657°$.
    (c) 0.1 M. $MgCl_2$, freezing point, $- 0.494°$.
    (d) A solution containing 1.5 g. of KCl in 100 g. of water begins to freeze at $- 0.684°$.

124. From the degree of ionization, calculate the ionization constant of each of the following weak electrolytes:
    (a) HCN, 0.1 M., 0.01 per cent; (b) H_2S, 0.1 M. ($H^+ + HS^-$), 0.07 per cent; (c) H_2CO_3, 0.1 M. ($H^+ + HCO_3^-$), 0.17 per cent; (d) HF, 0.1 m., 8.5 per cent; (e) NH_3+H_2O, 0.1 M. ($NH_4^+ + OH^-$), 1.34 per cent.

125. Calculate the value of the ionization constant of acetic acid according to the per cent ionization at each of the following concentrations: 1 M., 0.42 per cent; 0.1 M., 1.33 per cent; 0.01 M., 4.1 per cent; 0.001 M., 12.5 per cent.

126. Calculate the concentration of the hydrogen ion in solutions of the following acids from the numerical values of the ionization constants given in Appendix X, page 622:
(a) 0.5 M. $HC_2H_3O_2$;   (b) 0.1 M. $HClO$;   (c) 1 M. HF;
(d) 0.5 M. HNO_2; (e) 0.1 HIO.

127. Calculate the concentrations of hydrogen ions in each of the following solutions of acetic acid if enough sodium acetate is added to each solution to maintain the concentration of the acetate ion 1 M.:
(a) 0.1 M.; (b) 0.5 M.; (c) 1 M.

128. Calculate the concentration of sulfide ions in solutions containing the following concentrations of hydrogen ions: (a) 2 M.; (b) 0.5 M.;
(c) 0.1 M.; (d) 1×10^{-7} M.; (e) 1×10^{-10} M.

129. What is the concentration of the hydrogen ion in the solutions which result from the addition of 50 ml. of 2 N. HCl to each of the following solutions: (a) 50 ml. of 2 N. NaOH; (b) 50 ml. of 2 N. Na_2S; (c) 50 ml. of 2 N. NaCN; (d) 50 ml. of 2 N. Na_2CO_3; (e) 50 ml. of 2 N. NH_3.

130. From the solubility data in Appendix VIII, page 620, calculate the solubility products of the following substances: (a) AgCl; (b) AgBr;
(c) $BaSO_4$; (d) $PbCl_2$; (e) $Mg(OH)_2$.

131. From the solubility product data, Appendix IX, page 621, calculate the solubility in moles per liter of the following substances: (a) ZnS;
(b) AgI; (c) $BaCrO_4$; (d) Ag_2SO_4; (e) AgCN.

132. What is the maximum concentration of the carbonate ion that may be used in the precipitation of the calcium group of cations without precipitating magnesium carbonate if the concentration of the magnesium ion is 0.1 M.?

133. What is the maximum concentration of the hydroxide ion that may be present in a solution in which the concentration of the magnesium ion is 0.1 M.?

134. Calculate the maximum concentration of the chromate ion that may be used for the separation of barium and strontium ions in a solution which is 0.1 M. with respect to each of these ions.

135. Calculate the concentration of hydrogen ions required to regulate the sulfide ion concentration so as to effect the separation of cadmium and zinc ions in a solution in which they are each present in 0.1 M. concentration.

APPENDIX

I. UNITS OF MEASUREMENT

Length

1 kilometer	= 1000 meters (m.)	= 0.6214 mile
1 meter	= 100 centimeters (cm.)	= 39.37 inches
1 centimeter	= 0.3937 in.	
1 inch	= 2.54 cm.	

Volume

1 liter	= 1000 milliliters (ml.)	= 1.06 quarts, fluid
1 liter	= 1000.027 cubic centimeters (cc.)	
1 fluid ounce	= 29.5737 cc.	
1 cubic foot	= 28.32 liters	

Gram molecular volume of a gas at 0° and 760 mm. = 22.4 liters

Weight

1 gram (g.)	= weight of 1 ml. of water at 4°
1 kilogram (kg.)	= 1000 g. = 2.2 pounds avoirdupois (lb.)
1 pound	= 453.6 g.
1 ounce avoirdupois	= 28.35 g.
1 short ton	= 2000 lb.
1 long ton	= 2240 lb.
1 metric ton	= 1000 kg. = 2204.6 lb.

Temperature

0° centigrade	= freezing point of water = 32° Fahrenheit
100° centigrade	= boiling point of water = 212° Fahrenheit

Electricity

96,500 coulombs	= quantity of electricity required to deposit 1 g. equivalent of an element = 1 faraday
1 ampere	= 1 coulomb per second
1 coulomb	= quantity of electricity required to deposit 0.0011180 g. of silver from a solution of a silver salt
1 ohm	= unit of resistance. The resistance at 0° offered by a column of mercury 106.300 cm. in length and of such cross section that it weighs 14.4521 g.
1 volt	= unit of potential difference. The amount of the electromotive force required to cause a current to flow at the rate of 1 ampere through a resistance of 1 ohm

II. VAPOR PRESSURE OF WATER

Temperature, °C	Pressure, mm.	Temperature, °C	Pressure, mm.
0	4.6	30	31.8
5	6.5	31	33.7
10	9.2	32	35.7
11	9.8	33	37.7
12	10.5	34	39.9
13	11.2	35	42.2
14	12.0	36	44.6
15	12.8	37	47.1
16	13.6	38	49.7
17	14.5	39	52.4
18	15.5	40	55.3
19	16.5	45	71.9
20	17.5	50	92.5
21	18.6	55	118.0
22	19.8	60	149.4
23	21.1	65	187.5
24	22.4	70	233.7
25	23.8	75	289.1
26	25.2	80	355.1
27	26.7	85	433.6
28	28.4	90	525.8
29	30.0	100	760.0

III. VALENCES OF COMMON POSITIVE IONS

Valence 1	*Valence 2*	*Valence 3*
Ammonium, NH_4^+	Barium, Ba^{++}	Aluminum, Al^{+++}
Cuprous, Cu^+	Calcium, Ca^{++}	Antimony, Sb^{+++}
Hydrogen, H^+	Cupric, Cu^{++}	Bismuth, Bi^{+++}
Potassium, K^+	Ferrous, Fe^{++}	Chromic, Cr^{+++}
Silver, Ag^+	Lead, Pb^{++}	Ferric, Fe^{+++}
Sodium, Na^+	Magnesium, Mg^{++}	
	Mercuric, Hg^{++}	
	Stannous, Sn^{++}	
	Strontium, Sr^{++}	
	Zinc, Zn^{++}	

IV. NONMETAL OXIDES AND CORRESPONDING ACIDS AND SALTS

Element	Oxide	Acid			Salt
Nitrogen	N_2O_3	Nitrous	HNO_2	Nitrite	$NaNO_2$
	N_2O_5	Nitric	HNO_3	Nitrate	$NaNO_3$
Carbon	CO_2	Carbonic	H_2CO_3	Carbonate	Na_2CO_3
Sulfur	SO_2	Sulfurous	H_2SO_3	Sulfite	Na_2SO_3
	SO_3	Sulfuric	H_2SO_4	Sulfate	Na_2SO_4
Silicon	SiO_2	Metasilicic	H_2SiO_3	Metasilicate	Na_2SiO_3
	SiO_2	Orthosilicic	H_4SiO_4	Orthosilicate	Na_4SiO_4
Phosphorus	P_2O_3	Phosphorous	H_2HPO_3	Phosphite	Na_2HPO_3
	P_2O_5	Phosphoric	H_3PO_4	Phosphate	Na_3PO_4
Arsenic	As_2O_3	Arsenious	H_3AsO_3	Arsenite	Na_3AsO_3
	As_2O_5	Arsenic	H_3AsO_4	Arsenate	Na_3AsO_4
Boron	B_2O_3	Boric	H_3BO_3	Borate	Na_3BO_3
Chlorine	Cl_2O	Hypochlorous	$HClO$	Hypochlorite	$NaClO$
	Cl_2O_7	Perchloric	$HClO_4$	Perchlorate	$NaClO_4$
Manganese	MnO_3	Manganic	H_2MnO_4	Manganate	Na_2MnO_4
	Mn_2O_7	Permanganic	$HMnO_4$	Permanganate	$NaMnO_4$
Chromium	CrO_3	Chromic	H_2CrO_4	Chromate	Na_2CrO_4

V. ELECTROMOTIVE SERIES OF THE METALS *

These electrode potentials are expressed in volts, referred to the standard reference hydrogen electrode at 25° and unit activities.

Lithium	− 3.020	Iron, ferrous	− 0.440
Rubidium	− 2.990	Cadmium	− 0.402
Potassium	− 2.922	Cobalt	− 0.277
Barium	− 2.900	Nickel	− 0.250
Strontium	− 2.890	Tin, stannous	− 0.136
Calcium	− 2.870	Lead	− 0.126
Sodium	− 2.712	Hydrogen	0.000
Magnesium	− 2.340	Antimony, antimonyl	+ 0.212
Aluminum	− 1.670	Copper, cupric	+ 0.345
Manganese	− 1.050	Mercury, mercurous	+ 0.7986
Zinc	− 0.762	Silver	+ 0.7995
Chromium	− 0.710	Gold, auric	+ 1.420

* The data are from Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940.

VI. OXIDIZING AGENTS. TYPICAL HALF REACTIONS

Nonmetals

$$Cl_2 + 2\,\epsilon \longrightarrow 2\,Cl^-$$
$$S + 2\,\epsilon \longrightarrow S^{--}$$

Metal Ions

$$Fe^{+++} + 1\,\epsilon \longrightarrow Fe^{++}$$
$$2\,Hg^{++} + 2\,\epsilon \longrightarrow Hg_2^{++}$$
$$Cu^{++} + 2\,\epsilon \longrightarrow Cu$$

Oxyions in Acidic Solution

$$NO_3^- + 4\,H^+ + 3\,\epsilon \longrightarrow NO + 2\,H_2O$$
$$NO_3^- + 2\,H^+ + 1\,\epsilon \longrightarrow NO_2 + H_2O$$
$$NO_3^- + 10\,H^+ + 8\,\epsilon \longrightarrow NH_4^+ + 3\,H_2O$$
$$ClO_3^- + 6\,H^+ + 6\,\epsilon \longrightarrow Cl^- + 3\,H_2O$$
$$MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O$$
$$Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon \longrightarrow 2\,Cr^{+++} + 7\,H_2O$$
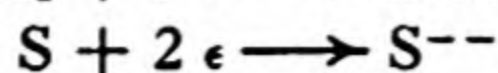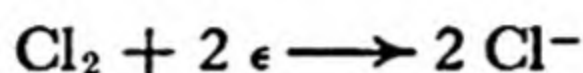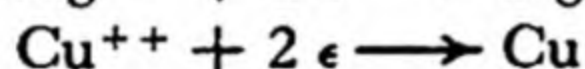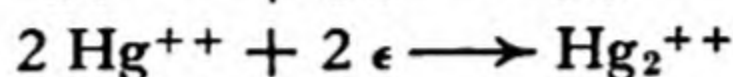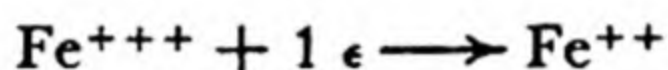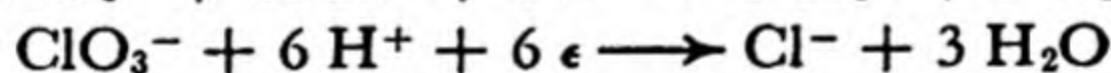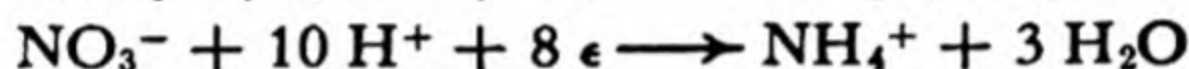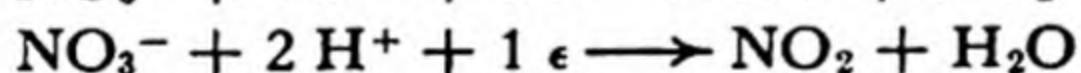
Molecular Oxidizing Agents in Acidic Solution

$$HClO + H^+ + 2\,\epsilon \longrightarrow Cl^- + H_2O$$
$$HNO_2 + H^+ + 1\,\epsilon \longrightarrow H_2O + NO$$
$$H_2SO_4 + 2\,H^+ + 2\,\epsilon \longrightarrow SO_2 + 2\,H_2O$$
$$H_2SO_4 + 8\,H^+ + 8\,\epsilon \longrightarrow H_2S + 4\,H_2O$$
$$H_2SO_3 + 4\,H^+ + 4\,\epsilon \longrightarrow S + 3\,H_2O$$
$$H_2O_2 + 2\,H^+ + 2\,\epsilon \longrightarrow 2\,H_2O$$

Oxyions in Basic Solution

$$ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-$$
$$Na_2O_2 + 2\,H_2O + 2\,\epsilon \longrightarrow 2\,Na^+ + 4\,OH^-$$
$$O_2 + 2\,H_2O + 4\,\epsilon \longrightarrow 4\,OH^-$$
$$MnO_4^- + 2\,H_2O + 3\,\epsilon \longrightarrow MnO_2 + 4\,OH^-$$
$$CrO_4^{--} + 4\,H_2O + 3\,\epsilon \longrightarrow Cr(OH)_4^- + 4\,OH^-$$
$$BiO^+ + H_2O + 3\,\epsilon \longrightarrow Bi + 2\,OH$$
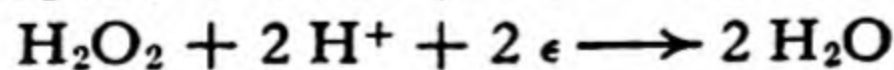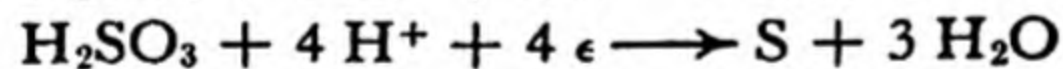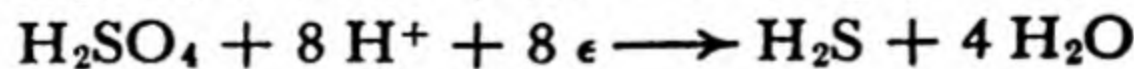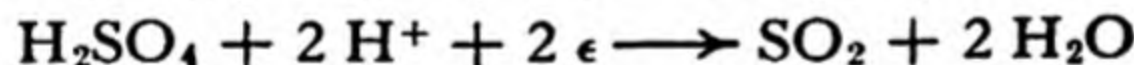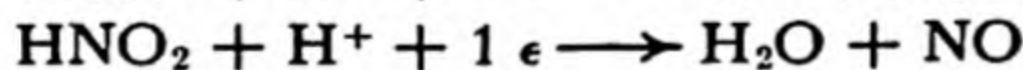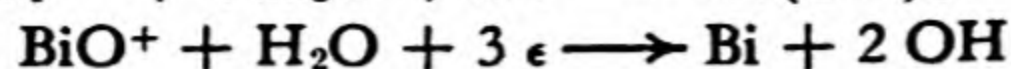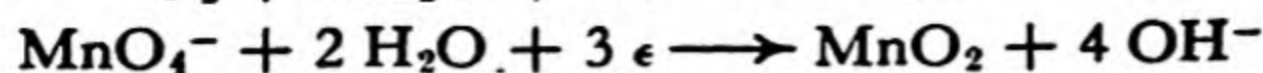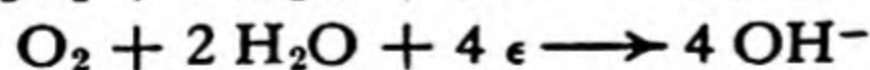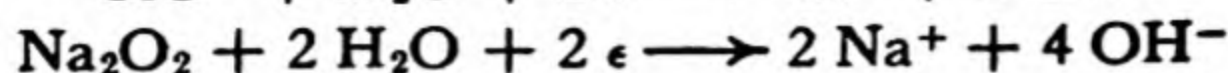
VII. REDUCING AGENTS. TYPICAL HALF REACTIONS

Metals

$$K \longrightarrow K^+ + 1\,\epsilon$$
$$Ca \longrightarrow Ca^{++} + 2\,\epsilon$$
$$Al \longrightarrow Al^{+++} + 3\,\epsilon$$
$$H_2 \longrightarrow 2\,H^+ + 2\,\epsilon$$
$$Cu \longrightarrow Cu^{++} + 2\,\epsilon$$

Low Valent Metal Ions

$$Hg_2^{++} \longrightarrow 2\,Hg^{++} + 2\,\epsilon$$
$$Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon$$
$$Sn^{++} + 6\,Cl^- \longrightarrow SnCl_6^{--} + 2\,\epsilon$$
$$CuCl_2^- \longrightarrow Cu^{++} + 2\,Cl^- + 1\,\epsilon$$

Simple Negative Ions

$$S^{--} \longrightarrow S + 2\,\epsilon$$
$$2\,I^- \longrightarrow I_2 + 2\,\epsilon$$
$$2\,Cl^- \longrightarrow Cl_2 + 2\,\epsilon$$
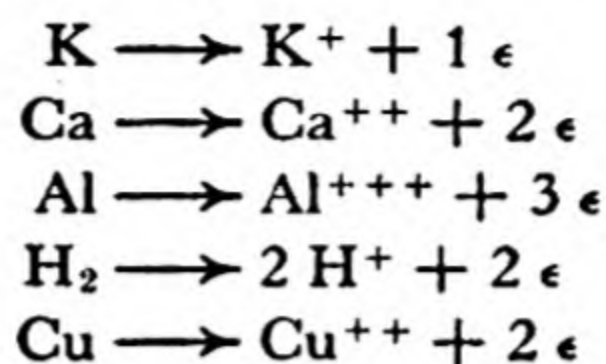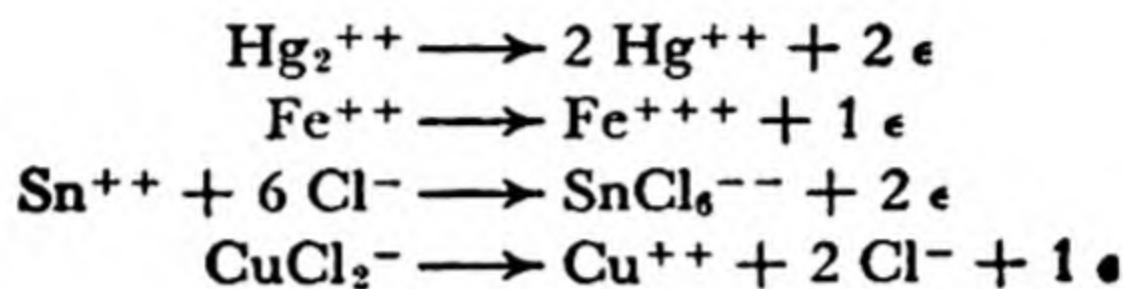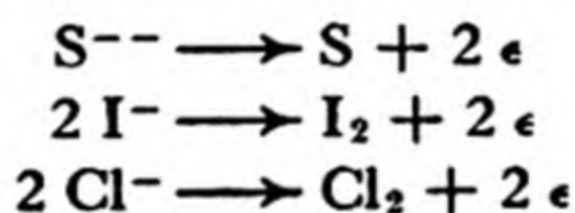
Nonmetals with Acidic Oxidizing Agents

$$P + 4\,H_2O \longrightarrow H_3PO_4 + 5\,H^+ + 5\,\epsilon$$
$$S + 4\,H_2O \longrightarrow SO_4^{--} + 8\,H^+ + 6\,\epsilon$$
$$I_2 + 6\,H_2O \longrightarrow 2\,IO_3^- + 12\,H^+ + 10\,\epsilon$$
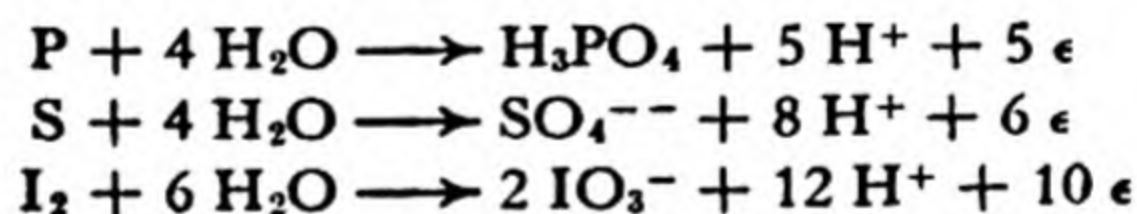
Nonmetals with Basic Oxidizing Agents

$$S + 8\,OH^- \longrightarrow SO_4^{--} + 4\,H_2O + 6\,\epsilon$$
$$P + 8\,OH^- \longrightarrow PO_4^{---} + 4\,H_2O + 5\,\epsilon$$
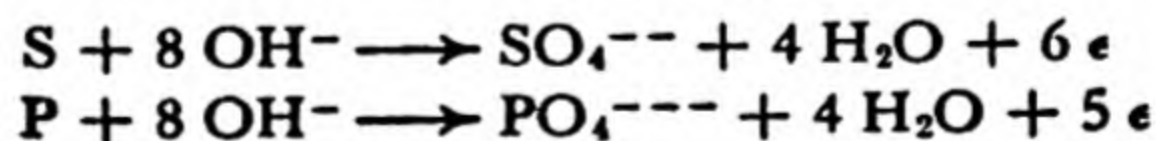
Oxycompounds in Basic Solution

$$Cr(OH)_4^- + 4\,OH^- \longrightarrow CrO_4^{--} + 4\,H_2O + 3\,\epsilon$$
$$MnO_2 + 4\,OH^- \longrightarrow MnO_4^{--} + 2\,H_2O + 2\,\epsilon$$
$$MnO_4^{--} \longrightarrow MnO_4^- + 1\,\epsilon$$
$$SO_3^{--} + 2\,OH^- \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon$$
$$Sn(OH)_4^{--} + 2\,OH^- \longrightarrow Sn(OH)_6^{--} + 2\,\epsilon$$
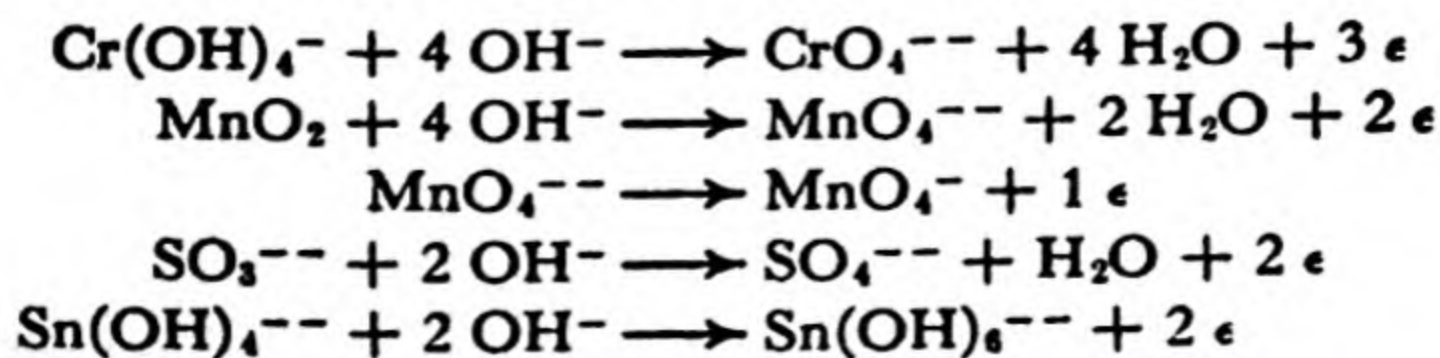
VIII. SOLUBILITIES OF SOME OF THE COMMON SALTS AND HYDROXIDES *

(Grams of anhydrous solute in 100 g. of water at 20° unless otherwise noted)

Chlorides

Ammonium chloride	37.2
Barium chloride	35.7
Calcium chloride (H_2O)$_6$	74.5
Lead chloride	0.993
Magnesium chloride (H_2O)$_6$	54.5
Potassium chloride	34.0
Silver chloride	1.5×10^{-4}
Sodium chloride	36.0

Iodides

Calcium iodide (100 g. of solution)	67.6
Lead iodide	0.068
Potassium iodide	144.0
Silver iodide	2.9×10^{-7}
Sodium iodide (H_2O)$_2$	178.7

Carbonates

Barium carbonate	2.2×10^{-3}
Calcium carbonate	1.4×10^{-3}
Lead carbonate	1.1×10^{-4}
Potassium carbonate	112.0
Sodium carbonate (H_2O)$_{10}$	21.5
Strontium carbonate	1.1×10^{-3}
Potassium bicarbonate	22.4
Sodium bicarbonate	9.6
Ammonium bicarbonate	21.0

Sulfates

Ammonium sulfate	75.0
Barium sulfate	2.4×10^{-4}
Calcium sulfate	0.208
Copper sulfate	20.7
Magnesium sulfate	34.6
Potassium sulfate	11.11
Sodium sulfate (H_2O)$_{10}$	19.4
Strontium sulfate	1.1×10^{-2}
Zinc sulfate	86.5

Bromides

Ammonium bromide	75.5
Barium bromide	104.0
Calcium bromide (H_2O)$_6$	143.0
Lead bromide	0.85
Magnesium bromide (H_2O)$_6$	96.5
Potassium bromide	65.2
Silver bromide	8.4×10^{-6}
Sodium bromide (H_2O)$_2$ (100 g. of solution)	47.5

Fluorides

Calcium fluoride	1.3×10^{-3}, 18°
Lead fluoride	0.064
Potassium fluoride	92.0, 18°
Silver fluoride	182.0, 15°
Sodium fluoride	4.22, 18°

Nitrates

Ammonium nitrate	192.0
Barium nitrate	9.2
Calcium nitrate	102.0, 0°
Lead nitrate	56.5
Magnesium nitrate (H_2O)$_6$	42.3
Potassium nitrate	31.6
Silver nitrate	122.0
Sodium nitrate	88.0
Strontium nitrate (H_2O)$_4$	70.5

Hydroxides

Barium hydroxide	3.89
Calcium hydroxide	0.165
Magnesium hydroxide	9×10^{-4}
Potassium hydroxide (H_2O)$_2$	112.0
Sodium hydroxide (H_2O)	109.0
Strontium hydroxide	0.41, 0°
Zinc hydroxide	2.2×10^{-4}

* The data are based primarily on *Handbook of Chemistry and Physics*, 25th edition, Chemical Rubber Publishing Company, Cleveland, 1941.

IX. SOLUBILITY PRODUCTS AT 20° *

It may be assumed without great error that the effective ion concentration in dilute, saturated solutions of slightly soluble substances, is equal to the total ion concentration.

Substance	Formula	Solubility Product
Aluminum hydroxide	$Al(OH)_3$	1.9×10^{-33}
Barium carbonate	$BaCO_3$	6.2×10^{-10}
Barium chromate	$BaCrO_4$	2×10^{-10}
Barium oxalate	BaC_2O_4	2×10^{-7}
Barium sulfate	$BaSO_4$	1×10^{-10}
Cadmium sulfide	CdS	1.4×10^{-28}
Calcium carbonate	$CaCO_3$	2×10^{-8}
Calcium chromate	$CaCrO_4$	2×10^{-2}
Calcium oxalate	CaC_2O_4	4×10^{-9}
Calcium sulfate	$CaSO_4$	3.5×10^{-6}
Chromic hydroxide	$Cr(OH)_3$	6.7×10^{-31}
Cobalt sulfide	CoS	1×10^{-26}
Cobalt sulfide	$CoS\alpha$	7×10^{-23}
Cupric sulfide	CuS	4×10^{-38}
Ferric hydroxide	$Fe(OH)_3$	1×10^{-38}
Ferrous hydroxide	$Fe(OH)_2$	1.6×10^{-14}
Ferrous sulfide	FeS	1×10^{-19}
Lead bromide	$PbBr_2$	7.8×10^{-6}
Lead chloride	$PbCl_2$	1.8×10^{-4}
Lead chromate	$PbCrO_4$	2×10^{-14}
Lead iodide	PbI_2	8.7×10^{-9}
Lead sulfate	$PbSO_4$	1.8×10^{-8}
Lead sulfide	PbS	1×10^{-29}
Magnesium carbonate	$MgCO_3$	1×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	2.8×10^{-11}
Magnesium ammonium phosphate	$MgNH_4PO_4$	2.5×10^{-13}
Manganous hydroxide	$Mn(OH)_2$	7.1×10^{-15}
Manganous sulfide	MnS	1.6×10^{-16}
Mercuric iodide	HgI_2	2.9×10^{-12}
Mercuric sulfide	HgS	1×10^{-53}
Mercurous chloride	Hg_2Cl_2	3×10^{-18}
Nickel sulfide	NiS	1.4×10^{-24}
Nickel sulfide	$NiS\alpha$	3×10^{-21}
Silver bromide	$AgBr$	3.3×10^{-13}
Silver chloride	$AgCl$	1.1×10^{-10}
Silver cyanide	$AgCN$	1×10^{-13}
Silver iodide	AgI	8.5×10^{-17}
Silver phosphate	Ag_3PO_4	1.8×10^{-18}
Stannous sulfide	SnS	8×10^{-29}
Strontium carbonate	$SrCO_3$	4.6×10^{-9}
Strontium chromate	$SrCrO_4$	5×10^{-5}
Strontium oxalate	SrC_2O_4	1.4×10^{-7}
Strontium sulfate	$SrSO_4$	7.2×10^{-9}
Zinc hydroxide	$Zn(OH)_2$	4×10^{-17}
Zinc sulfide	ZnS	4.5×10^{-24}

* The data are based primarily on *International Critical Tables*, McGraw-Hill Book Company, Inc., New York, 1926, and Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940.

X. IONIZATION CONSTANTS AT 25° *

Substance	Formula	Constant
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}
Boric acid	H_3BO_3	5.8×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
Bicarbonate ion	HCO_3^-	4.7×10^{-11}
Hydrocyanic acid	HCN	4×10^{-10}
Hydrofluoric acid	HF	7.2×10^{-4}
Hypobromous acid	$HBrO$	2×10^{-9}
Hypochlorous acid	$HClO$	5.6×10^{-8}
Hypoiodous acid	HIO	1×10^{-11}
Nitrous acid	HNO_2	4.5×10^{-4}
Phosphoric acid	H_3PO_4	7.5×10^{-3}
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}
Monohydrogen phosphate ion	HPO_4^{--}	1×10^{-12}
Hydrogen sulfide	H_2S	1.1×10^{-7}
Hydrosulfide ion	HS^-	1×10^{-15}
Water	H_2O	1×10^{-14}
Ammonia water	$NH_3(NH_4^+ + OH^-)$	1.8×10^{-5}

XI. ACIDITY–BASICITY CHART *

$$\text{Acid} \rightleftharpoons \text{Conjugate Base} + H^+. \quad K_a = \frac{[\text{Base}] \times [H^+]}{[\text{Acid}]}$$
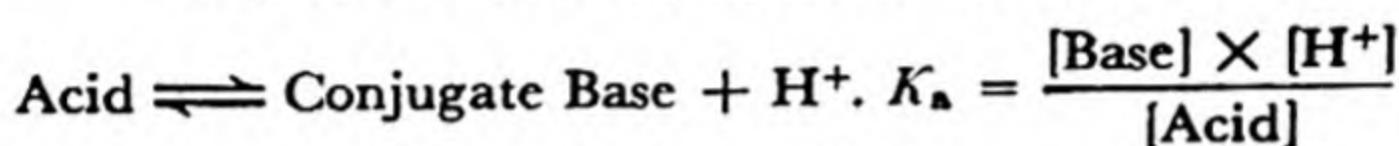
Acid	Conjugate Base	K_a
H_3PO_3	$H_2PO_3^-$	1.8×10^{-2}
H_2SO_3	HSO_3^-	1.2×10^{-2}
HSO_4^-	SO_4^{--}	1×10^{-2}
$\overline{Fe(H_2O)_6}^{+++}$	$\overline{Fe(H_2O)_5OH}^{++}$	6×10^{-3}
$\overline{Cr(H_2O)_6}^{+++}$	$\overline{Cr(H_2O)_5OH}^{++}$	1.5×10^{-4}
$Fe(H_2O)_5OH^{++}$	$Fe(H_2O)_4(OH)_2^+$	2×10^{-5}
$HC_2H_3O_2$	$C_2H_3O_2^-$	1.6×10^{-5}
$\overline{Al(H_2O)_6}^{+++}$	$\overline{Al(H_2O)_5OH}^{++}$	1.1×10^{-5}
H_2CO_3	HCO_3^-	4.3×10^{-7}
$\overline{Fe(H_2O)_4(OH)_2}^+$	$\overline{Fe(H_2O)_3(OH)_3} \downarrow$	4×10^{-7} (estimated)
$HCrO_4^-$	CrO_4^{--}	3.2×10^{-7}
H_2S	HS^-	1.1×10^{-7}
HSO_3^-	SO_3^{--}	1×10^{-7}
$H_2PO_4^-$	HPO_4^{--}	6.2×10^{-8}
$HClO$	ClO^-	5.6×10^{-8}
NH_4^+	NH_3	5.6×10^{-10}
HCN	CN^-	4×10^{-10}
$\overline{Zn(H_2O)_4}^{++}$	$\overline{Zn(H_2O)_3OH}^+$	2.6×10^{-10}
HCO_3^-	CO_3^{--}	4.7×10^{-11}
$\overline{Al(H_2O)_3(OH)_3} \downarrow$	$\overline{Al(H_2O)_2(OH)_4}^-$	4×10^{-13}
H_2O	OH^-	1×10^{-14}
HS^-	S^{--}	1×10^{-15}
$\overline{Cr(H_2O)_3(OH)_3} \downarrow$	$\overline{Cr(H_2O)_2(OH)_4}^-$	9×10^{-17}
OH^-	O^{--}	$< 10^{-36}$

Increasing Acidity ↑ (left column)   *Increasing Basicity* ↓ (middle column)

* Based primarily on Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*, The Macmillan Company, New York, 1940.

XII. PERIODIC SYSTEM BASED ON ATOMIC WEIGHTS (SHORT FORM)

Group → / Period ↓	0	I	II	III	IV	V	VI	VII	VIII
I		H 1.008							
II Short	He 4.0	Li 6.9	Be 9.0	B 10.8	C 12.0	N 14.0	O 16.0	F 19.0	
III Short	Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5	
IV Long	A 39.9	K 39.1	Ca 40.1	Sc 45.1	Ti 47.9	V 51.0	Cr 52.0	Mn 54.9	Fe 55.8 Co 58.9 Ni 58.7
		Cu 63.6	Zn 65.4						
V Long	Kr 83.7	Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Cb 92.9	Mo 96.0	Ma —	Ru 101.7 Rh 102.9 Pd 106.7
	Xe 131.3	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	
VI Long		Cs 132.9	Ba 137.4	La 138.9	Hf 178.6	Ta 180.9	W 184.0	Re 186.3	Os 191.5 Ir 193.1 Pt 195.2
	Rn 222	Au 197.2	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0	Po 210	—	
VII Incomplete		—	Ra 226.0	Ac 226?	Th 232.1	Pa 231	U 238.1		

Atomic weights are given to the first decimal place.

Fourteen elements are omitted from this classification. These elements together with lanthanum and hafnium are the *rare earths*.

Their symbols and atomic weights are: Ce, 140.1; Pr, 140.9; Nd, 144.3; Il, —; Sm, 150.4; Eu, 152.0; Gd, 156.9; Tb, 159.2; Dy, 162.5; Ho, 163.5; Er, 167.6; Tm, 169.4; Yb, 173.0; Lu, 175.0.

XIII. LOGARITHMS OF NUMBERS

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	7	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	6	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

XIII. LOGARITHMS OF NUMBERS (continued)

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8773	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

XIV. EXPONENTIAL NUMBERS

Large numbers are conveniently expressed as powers of the base 10. Thus, 3×10^4 means that 10 is raised to the fourth power, 10,000, and this number is multiplied by 3, giving 30,000. The same number may be written 30×10^3 or 0.3×10^5. The number, 6.064×10^{23} is equal to 606,400,000,000,000,000,000,000. Negative exponents are used to represent very small fractions. They represent the fraction resulting from the division of the coefficient by the number obtained when the base is raised to the power indicated. Thus, 3×10^{-5} represents $3/10 \times 10 \times 10 \times 10 \times 10$, or $3/100000$, or 0.00003. The multiplication of exponential numbers consists in multiplying the coefficients and adding the exponents.

$$3 \times 10^5 \times 3 \times 10^3 = 9 \times 10^8.$$
$$2 \times 10^{-6} \times 2 \times 10^{-8} = 4 \times 10^{-14}.$$

In division, the coefficients are divided and the exponents subtracted.

$$9 \times 10^{10} \div 3 \times 10^2 = 3 \times 10^8$$
$$8 \times 10^{-10} \div 4 \times 10^{-3} = 2 \times 10^{-7}.$$

For addition and subtraction, the numbers must be converted to the same power of the base. The coefficients are then added or subtracted in the usual manner. This is equivalent to "lining up the decimal point."

$$3.4 \times 10^5 + 2.6 \times 10^4 =$$
$$3.4 \times 10^5 + 0.26 \times 10^5 = 3.66 \times 10^5.$$

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PERIODIC CLASSIFICATION OF THE ELEMENTS BASED ON ATOMIC NUMBERS

I	II	III-B	IV-B	V-B	VI-B	VII-B	VIII-B			I-B	II-B	III	IV	V	VI	VII	VIII
																	He 2
												B 5	C 6	N 7	O 8	F 9	Ne 10
												Al 13	Si 14	P 15	S 16	Cl 17	A 18
			Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
				Cb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
					W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	Rn 86

Transition Elements (Fe 26 … Ni 28, Ru 44 … Pd 46, Os 76 … Pt 78)

e, 58; Pr, 59; Nd, 60; Il, 61; Sm, 62; Eu, 63; Gd, 64; Tb, 65; Dy, 66; ͯ the rare earths. They contain the same number of valence electrons,